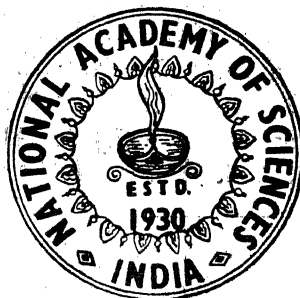


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PART III



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PART III

**"HUMIFICATION OF SAINJI IN THE SOIL OF AGRA
DISTRICT AND ESTIMATED VARIATIONS OF THE
INORGANIC CONSTITUENTS AT DIFFERENT
PERIODS OF HUMIFICATION"**

By

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Chemistry Department, Agra College, Agra

Received on 1st Sept. 1956.

INTRODUCTION

It is a well-known fact that climatic conditions, specially rainfall and temperature, exert an important influence on the amounts of nitrogen and organic matter found in soils. Jenny (1928) observed that the decomposition of organic matter is much more accelerated in warm regions than in cooler ones. A sandy soil usually carries less organic matter and nitrogen than heavy soils, probably owing to lower moisture content and more ready oxidation that occurs in lighter soil. The lime content may also exert an influence upon the accumulation and the activity of soil organic matter and its nitrogen content, though there may be several more interlocked factors to control the level of organic matter and nitrogen.

Humification increases the organic acids and acidoid contents of the humus complex, while mineralisation tends to decrease these acids and increase the basoid

contents of humus. Since the plants or the weeds contain both organic and inorganic constituents it should evidently follow that during the process of humification the soil should be enriched not only in organic humus but also in the total mineral matter obtained by the decomposition of the plants, unless, of course, the inorganics are leached out in the lower layers of the soil.

In view of the fact that Agra is in a dry and hot zone, and its soil is poor in organic matter, we have attempted to study quantitatively the variations in the total mineral constituents of its soil resulting from the humification of a well-known leguminous weed (Sainji) in the so called typical 'Dumat' soil of the district. The variations in SiO_2 , Fe, Al, Ca, Mg, K & P_2O_5 have been studied in relation to the humification of Sainji at different periods of humification and the data are being communicated through this paper.

EXPERIMENTAL

Soil and Sainji were mixed in ratio 19:1. The dust was previously removed from the weed and it was chopped into very small pieces and powdered. The whole quantity of the treated soil was macerated with distilled water and left under the shade to humify. The moisture content of the soil was maintained at a 10% level by weighing in Beringer balance on alternate days and by adding the required amount of distilled water to it. The soil was then allowed to remain under aerobic condition. At the end of certain definite periods the samples were taken and air-dried. The soil samples thus obtained were properly sieved for various estimations. All these experiments were performed in duplicate and the result shown herein is the average of these two.

Inorganic Constituents of the weed were estimated by the methods suggested by A. O. A. C. (1945). The inorganic constituents of the humified and original untreated soil were estimated by the standard methods suggested by Piper (1947):

TABLE No. I
*Percentage inorganic constituents during
humification (on ignition basis)*

Soil Constituents :	Period of Humification in months				
	0	2nd	3rd	4th	5th
(Soil & Weed)					
SiO_2	91.37	93.460	92.6600	92.2300	91.3500
Fe_2O_3	3.113	2.0790	3.0500	...	2.8960
Al_2O_3	2.425	...	2.7894	2.6559	...
CaO	0.7204	0.7832	0.6705	0.7834	0.6732
MgO	1.111	0.9970	1.1550	1.0550	1.1340
K_2O	1.169	0.4334	0.2981	0.5299	0.3907
Loss on Ignition	6.6273	4.246	4.156	3.736	4.246

DISCUSSION

From the analytical result given in the table I, it becomes evident that the proportion of the mineral constituents undergoes irregular variation during the humification of the raw organic matter (Sainji) added to the soil. In the case of SiO_2 , Fe_2O_3 , Al_2O_3 , CaO , MgO , the variations are either positive or negative from month to month.

The variations in K_2O during humification of Sainji definitely show that the estimated K_2O is less than the original soil plus organic matter at all stages of humification. The slight increase of CaO and MgO may be due to the limitations of the experimental methods employed and the presence of organic matter in such a complex system as humified soil.

The positive variations in Silica are probably due to the changes in the surface properties of the Colloidal silica at different periods of humification or they are due to the displacement effects brought about in the Silica units. It is interesting to observe that when the percentage of silica increases, the amount of Fe_2O_3 and Al_2O_3 are decreased, showing thereby that either iron or aluminium is absorbed by the colloidal silicic acid in different amounts at different stages of humification or they enter into the lattice frame of the clay minerals in variable amount during the process of humification. The lowering of K_2O may be due to the adsorption of potassium by the humic acid or humus which increases in the soil during the humification of raw organic matter (sainji).

SUMMARY

The changes in K_2O during humification of Sainji definitely show that the estimated K_2O is less than the original soil plus organic matter which may be due to the adsorption of potassium by the humic acid or humus. The positive variations in silica and the corresponding decrease in the amounts of Fe_2O_3 and Al_2O_3 may be due to the adsorption of either Iron or Aluminium by colloidal silicic acid in different amounts at various stages of humification.

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ROLE OF $\text{SiO}_2/\text{R}_2\text{O}_3$ RATIO OF THE WEEDS AND THE RESIDUAL ORGANIC MATTER ON THE TOTAL CATION EXCHANGE CAPACITY OF THE HUMIFIED "DUMAT" SOIL OF AGRA DISTRICT

By

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Received on 24th September, 1956

Parker and Pate (1926) observed that the exchangeable base in the soil appears to remain in the colloidal material, because a good correlation between $\text{SiO}_2/\text{R}_2\text{O}_3$ ratios of soil colloids and their contents of exchangeable bases was obtained. Williams (1932) studied the contribution of clay and organic matter to the base-exchange capacity and showed that the base-exchange capacity was the most complicated function of clay content than is merely given by the ratio $\text{SiO}_2/\text{R}_2\text{O}_3$ and further suggested that the chemical characteristics of structural influence was probably involved in the base-exchange phenomenon. The relation between the organic matter in the soil and base-exchange capacity has been studied by many workers. McGeorge (1934) studied the base-exchange in presence of plant residues and green manures and came to the definite conclusion that base-exchange capacity increases in presence of these substances. Smolik (1933) observed that the Ligno-humus constituents of different soils do not show the same exchange capacity and it quickly rises with progressive humification. Miller and Co-workers (1936) observed that the decomposition of leguminous materials increases the exchange capacity of the Dickenson fine sandy loam more than the non-leguminous bodies. Baver (1930) studied the effect of organic matter on several physical properties of soils and observed that exchange capacity of humus varies between wide limits but usually is in the range of 100 to 300 M. E. per 100 grams.

In view of the foregoing references it is obvious that opinion regarding the relation of base-exchange property, and $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio should be further elaborated by more extensive data. With this end in view we have carried out some experiments on the humification of one leguminous weed, Chakwad, and two non-leguminous weeds—Chhota Dahatura and Anjana (Grass) in the 'Dumat' soil of Agra district to determine the nature of correlation observed between variations in $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio and the residual organic matter against the changes in cation exchange capacity brought about by the humification of these weeds for a period of 16 weeks.

EXPERIMENTAL

The dirt was removed from the weeds and they were crushed, pulverised and sieved through 100 mesh sieve. The raw organic matter in this form was mixed with the soil in the ratio of 20 parts of soil to one part by weight of weeds. The whole quantity was macerated with distilled water and left under the shade to humify. The moisture content of the soil was maintained at 15% by weighing in a Beringer's balance on alternate days and adding required amount of distilled water. At the

end of 16 weeks soil samples were taken out and air dried. The soil samples thus obtained were properly sieved (100 mesh). The average of the four replicates is given in the table. Inorganic constituents of the weeds were estimated by the methods suggested by A. O. A. C. (1945). Total Cation exchange capacity was determined by the method suggested by Piper (1947). Organic carbon was determined by Walkley's (1935) rapid titration method.

TABLE No. 1

Analysis of soil and organics added for humification

	Soil Sample	Chakwad	Chhota Dahatura	Anjana
Loss on Ignition	3.803%	83.058%	80.6926	48.802%
Sand	84.21%	3.6592%	5.523%	38.1712%
Alkali Soluble Silica	---	0.3572%	1.379%	4.3532%
Fe ₂ O ₃	2.764%	0.144%	0.3120%	0.8576%
CaO	1.933%	3.116%	3.063%	0.9379%
MgO	0.1241%	0.4994%	0.7893%	0.6093%
Al ₂ O ₃	6.206%	5.308%	3.287%	1.2233%
K ₂ O	0.453%	1.832%	4.388%	1.2075%
P ₂ O ₅	0.1992%	0.4200%	0.4608%	0.2764%
SiO ₂ /R ₂ O ₃ ratio	---	1.265	3.373	41.04

TABLE No. 2

Changes in total Cation exchange capacity in the 'Dumat' soil of Agra district on humifying the weeds (For 16 weeks)

Soil Sample	Total Cation Exchange capacity %	Organic carbon%	SiO ₂ /R ₂ O ₃ ratio of the weed taken for humification
Untreated Soil	7.5 m.e.	0.1932%	---
Humified with Chakwad (Legume)	8.35 m.e.	0.8073%	1.265
Humified with Chhota Dahatura (Non-legume)	11.4 m.e.	0.9428%	3.373
Humified with Anjana (Non-legume)	13.7 m.e.	0.6151%	41.04

DISCUSSION

From the data given in the table No. 2, the following important observations can be made regarding the variations in the total cation exchange capacity, $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio of the weeds and also the residual percentage of organic carbon left in the soil after 16 weeks of humification.

The total cation exchange capacity of the soil after humification does not depend upon the leguminous or non-leguminous nature of the weeds as observed by Miller & Co-workers (1936). This observation is borne out by the fact that Chakwad which is leguminous has the least cation exchange capacity (8.35 m.e.) as against Chhota Dahatura (11.4 m.e.) and Anjana (13.7 m.e.) which are non-leguminous. Our observations clearly show that the cation exchange capacity is definitely increased by the decomposition of weeds and it is also interesting to note that the total exchange capacity of the humified soil varies in the order of the $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio of the weeds which were humified in the soil. Both these observations are in agreement with those of Parker and Pate (1926), McGeorge (1934), and Smolik (1933).

Another interesting observation is the variation of total cation exchange capacity in relation to the changes in the percentage of residual organic carbon (organic matter) and $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio of the weeds. In the case of Chakwad and Chhota Dahatura the total cation exchange capacity increased with the residual percentage of carbon in the humified soil but this order broke down in the case of Anjana, where the residual carbon was the least but the total cation exchange capacity was the highest. The foregoing observation confirms the view that cation-exchange capacity must be a very complicated function of the characteristics of the humus complex and also the ratio $\text{SiO}_2/\text{R}_2\text{O}_3$ as had been suggested by Williams (1932). It appears from our data that $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio of the decomposing plants and weeds is no less important a factor than the organic humus constituents to increase the total cation exchange capacity of the soil (cf. Anjana grass). The total cation exchange capacity resulting from the humification of Anjana grass does not fit in with the observation of Baver (1930) that the base exchange capacity increases with the humus content only, and hence we conclude that the cation exchange capacity does not depend either on humus characteristics or $\text{SiO}_2/\text{R}_2\text{O}_3$ taken as single factors but it depends on the relative predominance of one upon the other.

According to the observations of Parker and Pate (1926) the soil colloids expressed in terms of $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio could be correlated with the exchangeable bases. In our observations the ratio of $\text{SiO}_2/\text{R}_2\text{O}_3$ of the weeds (vide curve) are similarly related. From this it can be concluded that the colloidal silica and R_2O_3 forming the clay complex with organic matter come in greater proportion from the decomposition of the plants and weeds in the soil. The mineral contents of the soil therefore seem to contribute less than the plants towards the formation of colloidal clay complex.

SUMMARY

One legume-Chakwad (*Cassia obtusifolia*) and two non-legumes-Chhota Dahatura (*Xanthium strumarium*) and Anjana (*Cenchrus ciliaris*) were humified (for 16 weeks) in the Dumat soil of Agra district and the changes in total cation exchange capacity, residual organic carbon and $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio of the weeds were studied.

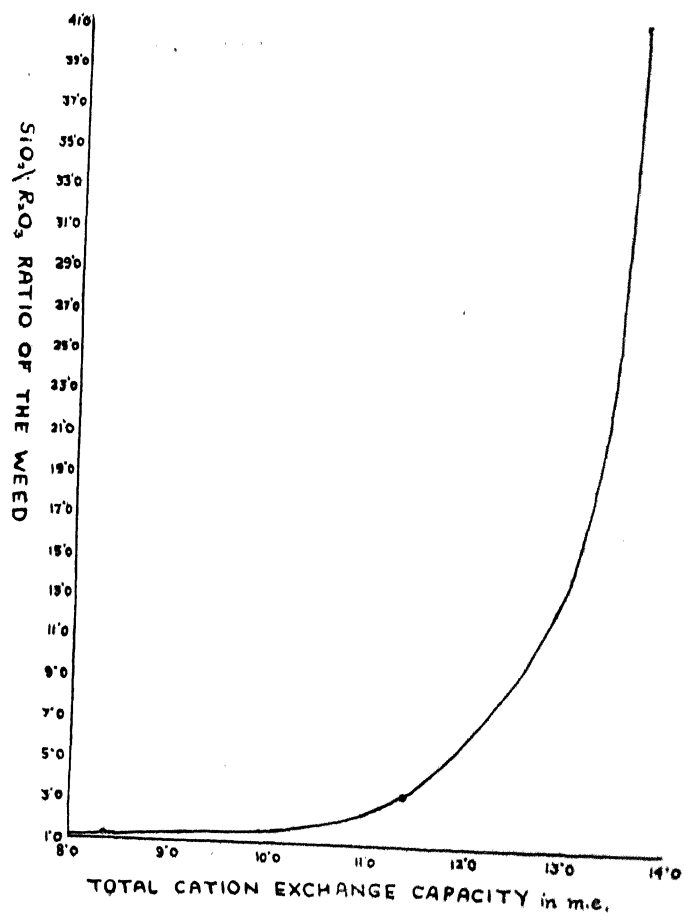
It has been observed that in case of Chakwad and Chhota Dahatura the total cation exchange capacity increased with the residual percentage of organic carbon in

humified soils, but this order broke down in case of Anjana where the residual carbon was the least but the total cation exchange capacity was the highest. This may be due to the high $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio of the Anjana. A correlation between the $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio of the weeds and total cation exchange capacity has been observed and it has been suggested that the total cation exchange capacity depends upon the relative preponderance of $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio over the humus contents or vice versa.

The total cation exchange capacity changed in the same order with the $\text{SiO}_2/\text{R}_2\text{O}_3$ ratio of the weeds. It appears from this observation that the colloidal clay humus is mainly formed from the silica of the decomposing weeds and plants, the contribution of the soil clay minerals being proportionately less.

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AN X-RAY STUDY OF THE STRUCTURE OF O-PHTHALIC ANHYDRIDE

By

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(Communicated by Prof. K. Banerjee)

(Read at the Annual Session on 29th December 1954)

ABSTRACT

From single crystal rotation photographs taken about the three crystallographic axes, the axial lengths of o-Phthalic Anhydride crystal have been found to be $a=7.86 \text{ \AA}$, $b=14.18 \text{ \AA}$ and $c=5.904 \text{ \AA}$.

From Weissenberg photographs about the three axes the space group is found to be either $D_{2h}^{16} - P_{nma}$ or $C_{2v}^9 - P_{na}$ depending upon whether the crystal possesses a centre of symmetry or not.

O-Phthalic Anhydride with a molecular formula $C_8H_4O_3$ is an Aromatic compound used as an intermediate for dyestuffs of Pyronine or Phthalein class and also for synthesis of Anthraquinones and many industrial products. Its complete structure determination by x-ray diffraction method has not yet been taken up. Morphological studies of crystals of o-Phthalic Anhydride were carried out by Groth¹ (1910) and Williams, van Meter & McCrone² (1952). It was found that the crystal belonged to the orthorhombic class. Becker & Jancke³ (1921) found the values of axial parameters to be $a=7.74 \text{ \AA}$, $b=13.66 \text{ \AA}$ and $c=5.86 \text{ \AA}$ from x-ray spectroscopic data. Using a more careful powder diffraction method Williams, Van Meter and McCrone found these as $a=7.90 \text{ \AA}$, $b=14.16 \text{ \AA}$ and $c=5.94 \text{ \AA}$ with a tetramolecular unit cell. The present work includes the measurement of axial lengths from single crystal rotation photographs taken about the three crystallographic axes and from the systematic absences observed in the normal beam Weissenberg photographs about the three crystallographic axes. Two probable space groups are suggested.

Single crystals of requisite size were obtained by laboratory recrystallisation from slow evaporation of a solution of o-Phthalic Anhydride in benzene. Rotation photographs of the single crystals were taken on a cylindrical camera using copper K-radiation from Philips sealed tube running at 45 kV and 15 mA. The axial parameters were found to be $a=7.86 \text{ \AA}$, $b=14.18 \text{ \AA}$ and $c=5.904 \text{ \AA}$. The density of o-Phthalic Anhydride was found to be 1.494 gm cm^{-3} by Williams, Van Meter & McCrone and using this value of density the number of formula weights per unit cell is found to be 4.

Well exposed zero layer normal beam Weissenberg photographs about the three crystallographic axes and equi-inclination photograph for the first layer line about the c-axis were taken on a Unicam Weissenberg Camera of diameter 57.3 mm. The spots were indexed by drawing the necessary Weissenberg charts. The visual estimates of the observed spots in the zero layer normal beam Weissenberg photographs about the three crystallographic axes and in the photograph for the first layer line about the c-axis are given in Tables I, II, III and IV.

The following systematic absences were observed :

- (1) hkl planes - All reflections present
- (2) hOl planes - Reflections with $h \neq 2n$ absent
- (3) Okl planes - Reflections with $k + l \neq 2n$ absent.

These conditions suggest that the space group of o-Phthalic Anhydride is

TABLE I

List of planes for the observed spots in the Weissenberg photograph about [100] axis, zero layer line.

(0 2 0)	(0 2 2)	(0 5 3)	(0 1 5)
(0 4 0)	(0 4 2)	(0 7 3)	(0 3 5)
(0 6 0)	(0 6 2)	(0 9 3)	(0 7 5)
(0 12 0)	(0 8 2)	(0 11 3)	(0 9 5)
(0 16 0)	(0 10 2)	(0 13 3)	(0 11 5)
	(0 12 2)	(0 15 3)	
(0 1 1)	(0 14 2)		
(0 3 1)	(0 16 2)	(0 2 4)	(0 2 6)
(0 5 1)		(0 4 4)	(0 4 6)
(0 9 1)	(0 0 2)	(0 6 4)	(0 6 6)
0 11 1	(0 0 4)	(0 8 4)	(0 8 6)
0 13 1	(0 0 6)	(0 10 4)	(0 10 6)
0 15 1		(0 12 4)	
0 17 1	(0 1 3)	(0 14 4)	
	(0 3 3)		

TABLE II

List of planes for the observed spots in the Weissenberg photograph about [010] axis, zero layer line.

(0 0 2)	(2 0 1)	(4 0 1)	(6 0 3)
(0 0 4)	(2 0 2)	(4 0 2)	(6 0 4)
(0 0 6)	(2 0 3)	(4 0 3)	(6 0 6)
	(2 0 4)	(4 0 4)	
(2 0 0)	(2 0 5)	(4 0 5)	(8 0 1)
(4 0 0)	(2 0 6)	(4 0 6)	(8 0 2)
(6 0 0)	(2 0 7)		(8 0 3)
(8 0 0)		(6 0 1)	(8 0 4)
		(6 0 2)	

TABLE III

List of planes for the observed spots in the Weissenberg photograph about $[001]$ axis, zero layer line

(1 1 0)	(2 4 0)	(3 8 0)	(4 14 0)
(1 2 0)	(2 5 0)	(3 9 0)	(4 15 0)
(1 3 0)	(2 6 0)	(3 10 0)	
(1 4 0)	(2 8 0)	(3 11 0)	(5 1 0)
(1 5 0)	(2 9 0)	(3 12 0)	(5 2 0)
(1 6 0)	(2 10 0)	(3 13 0)	(5 3 0)
(1 7 0)	(2 11 0)	(3 14 0)	(5 4 0)
(1 8 0)	(2 12 0)	(3 15 0)	(5 5 0)
(1 9 0)	(2 13 0)		(5 6 0)
(1 10 0)	(2 14 0)	(4 1 0)	(5 9 0)
(1 11 0)	(2 15 0)	(4 2 0)	(5 10 0)
(1 12 0)	(2 16 0)	(4 3 0)	(5 11 0)
(1 13 0)		(4 4 0)	(5 13 0)
(1 14 0)	(3 1 0)	(4 5 0)	
(1 15 0)	(3 2 0)	(4 6 0)	(6 1 0)
	(3 3 0)	(4 7 0)	(6 2 0)
(2 1 0)	(3 4 0)	(4 8 0)	(6 3 0)
(2 2 0)	(3 5 0)	(4 9 0)	(6 4 0)
(2 3 0)	(3 6 0)	(4 10 0)	(6 5 0)
	(3 7 0)	(4 12 0)	(6 6 0)

TABLE IV

List of planes for the observed spots in the Weissenberg photograph about $[001]$ axis, first layer line

(0 3 1)	(1 1 1)	(2 0 1)
(0 5 1)	(1 2 1)	(4 0 1)
(0 9 1)	(1 3 1)	(6 0 1)
(0 11 1)	(1 4 1)	(8 0 1)
(0 13 1)	(1 5 1)	
	(1 6 1)	

either $D_{2h}^{16} - P_{nma}$ or $C_{2v}^8 - P_{na}$ depending on whether the crystal possesses a centre of symmetry or not.

Further work on the determination of crystal structure of *o*-Phthalic Anhydride by Fourier Analysis is in progress.

The author expresses his thanks to Prof. K. Bangrjee, D.Sc., F.N.I., for suggesting the problem and for guidance, to Mr. R. K. Sen and Mr. B. V. R. Murty for their valuable help in the progress of this work.

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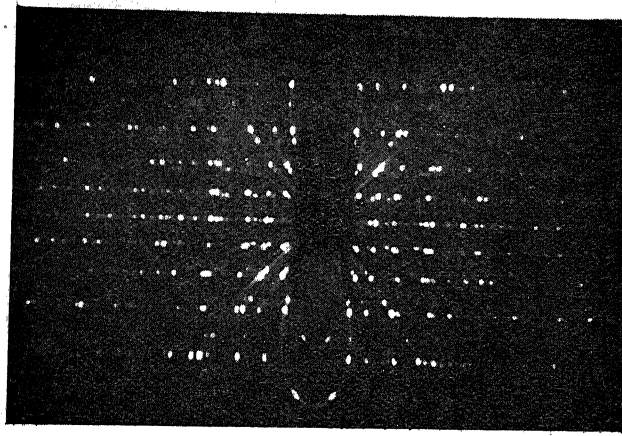


Plate 1. Rotation picture of O-Phthalic Anhydride about $[100]$ axis.

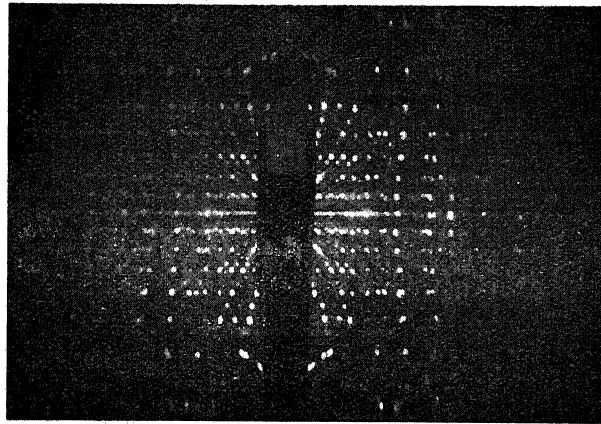


Plate 2. Rotation picture of O-Phthalic Anhydride about $[010]$ axis.

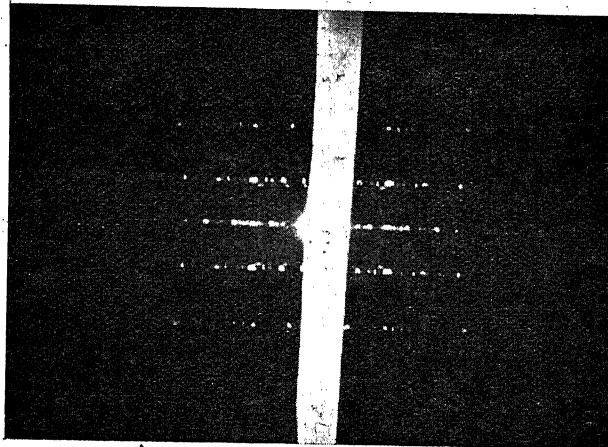


Plate 3. Rotation picture of O-Phthalic Anhydride about $[001]$ axis.

THEORY OF HYDROGEN HALIDES

By

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(Communicated by Dr. K. Majumdar)

(Received on 17th February, 1956)

INTRODUCTION

Several attempts have been made on the theoretical treatment of Hydrogen halides.

As a crude model, a Hydrogen halide HX can be imagined as a system in which a proton is embedded in the electronic cloud of the negative halogen ion X^- . This model has been very widely used in the theoretical treatments, both classical as well as semi-quantum mechanical.

Among the classical calculations, mention may be made of the work of Born and Heisenberg¹, Wall², Briegleb³, Davies^{4,5} and Moller⁶. In these the energy expression chiefly consists of an ionic attractive term, polarization terms, and a repulsion term. (See also Pauling⁷).

Approximate quantum mechanical investigations have been made by Pauling⁸, Fajans and Bauer⁹, Lovera¹⁰, and Johnston and Arnold¹¹. Platt¹² has used a slightly different model. Instead of the ion, he assumed that the proton is embedded in the electronic cloud of the united atom.

More detailed investigations have been carried out by Kirkwood¹³, Gombás and Neugebauer¹⁴, Horváth^{15,16,17,18}, Néray^{19,20}, and Gáspár and Kónya²¹.

In recent years complete wave mechanical treatments have also been given²²⁻²⁷.

ANOTHER TREATMENT

In the present paper we propose to give a semi-quantum mechanical treatment of Hydrogen halides. For the attractive term, we will take the usual ionic $-e^2/r$. But for the repulsive energy, we will make use of certain wave mechanical calculations due to Unsöld²⁸, Brück²⁹ and Van Leeuwen³⁰. They have shown that the repulsion energy due to the perturbation of a point charge, for the various closed shells is given by the following expressions, where

ze - Effective nuclear charge

a - Bohr radius

ϵ - Electronic charge; to avoid confusion with the exponential e this symbol has been used rather than the customary c .

For K shell:

$$\frac{2\epsilon^2 z}{a} \left[\frac{2}{r}, \frac{a}{2z} + 1 \right] \exp. \left(- \frac{2z}{a} r \right) \quad \dots (1)$$

For L shell :

$$\frac{\epsilon^2 z}{a} \left[\frac{8}{r} \cdot \frac{a}{z} + 6 + 2r \cdot \frac{z}{a} + \frac{1}{2} \cdot r^2 \left(\frac{z}{a} \right)^2 \right] \exp. \left(-\frac{z}{a} r \right) \dots (2)$$

For M shell :

$$\begin{aligned} & \frac{\epsilon^2 z}{18a} \left[\frac{96}{r} \left(\frac{3a}{2z} \right) + 80 + 32r \left(\frac{2z}{3a} \right) + 10r^2 \left(\frac{2z}{3a} \right)^2 \right. \\ & \left. + \frac{1}{3} r^3 \left(\frac{2z}{3a} \right)^3 + \frac{5}{6} r^4 \left(\frac{2z}{3a} \right)^4 \right] \exp. \left(-\frac{2z}{3a} r \right) \dots (3) \end{aligned}$$

For N shell :

$$\begin{aligned} & \frac{\epsilon^2 z}{80a} \left[\frac{320}{r} \cdot \frac{2a}{z} + 280 + 120r \left(\frac{z}{2a} \right) + 40r^2 \left(\frac{z}{2a} \right)^2 \right. \\ & \left. + 7r^4 \left(\frac{z}{2a} \right)^4 - \frac{13}{9} r^5 \left(\frac{z}{2a} \right)^5 + \frac{7}{36} r^6 \left(\frac{z}{2a} \right)^6 \right] \exp. \left(-\frac{z}{2a} r \right) \dots (4) \end{aligned}$$

For O shell :

$$\begin{aligned} & \frac{\epsilon^2 z}{18000a} \left[\frac{57600}{r} \cdot \frac{5a}{2z} + 51840 + 23040r \cdot \left(\frac{2z}{5a} \right) \right. \\ & + 7920r^2 \left(\frac{2z}{5a} \right)^2 - 360r^3 \left(\frac{2z}{5a} \right)^3 + 23040r^4 \left(\frac{2z}{5a} \right)^4 \\ & - 968r^5 \left(\frac{2z}{5a} \right)^5 + 252r^6 \left(\frac{2z}{5a} \right)^6 - 29r^7 \left(\frac{2z}{5a} \right)^7 \\ & \left. + \frac{3}{2} r^8 \left(\frac{2z}{5a} \right)^8 \right] \exp. \left(-\frac{2z}{5a} r \right) \dots (5) \end{aligned}$$

We make use of the ionic model of HX described above. In negative ions of F, Cl, Br and I, the outer closed shells are L, M, N, and O respectively. Thus the energy expressions for the various hydrogen halides can be put as follows.

For HF :

$$U = -\frac{\epsilon^2}{r} + \text{expression (2)} \dots (6)$$

For HCl :

$$U = -\frac{\epsilon^2}{r} + \text{expression (3)} \dots (7)$$

For HBr :

$$U = -\frac{\epsilon^2}{r} + \text{expression (4)} \dots (8)$$

For HI :

$$U = -\frac{\epsilon^2}{r} + \text{expression (5)} \dots (9)$$

For determining the effective nuclear charge ze , we utilize the condition :

$$\left(\frac{dU}{dr} \right)_{r=r_0} = 0$$

Differentiating equations (6), (7), (8) and (9) and putting

$$R_n = \frac{2z}{na} \cdot r_0$$

we get the following equations.

For HF :

$$1 - e^{-R_2} \left[8 + 8R_2 + 4R_2^2 + R_2^3 + \frac{1}{2}R_2^4 \right] = 0$$

For HCl :

$$1 - e^{-R_3} \left[48 + 48R_3 + 24R_3^2 + 6R_3^3 + (9/2)R_3^4 - (3/2)R_3^5 + (5/12)R_3^6 \right] = 0$$

For HBr :

$$1 - \frac{e^{-R_4}}{6} \left[48 + 48R_4 + 24R_4^2 + 6R_4^3 + 6R_4^4 - (21/5)R_4^5 + (32/15)R_4^6 - (47/120)R_4^7 + (7/240)R_4^8 \right] = 0$$

For HI :

$$1 - \frac{e^{-R_5}}{7200} \left[57600 + 57600R_5 + 28800R_5^2 + 7200R_5^3 + 9000R_5^4 - 92520R_5^5 + 27880R_5^6 - 2480R_5^7 + 455R_5^8 - 41R_5^9 + (3/2)R_5^{10} \right] = 0$$

From these equations we can find out R_2 , R_3 , R_4 and R_5 .

Further from the condition

$$\left(\frac{d^2U}{dr^2} \right)_{r=r_0} = k_0$$

it can be shown that

for HF :

$$k_0 = -\frac{2e^2}{r_0^3} + \frac{e^2}{r_0^3} e^{-R_2} \left[16 + 16R_2 + 8R_2^2 + 3R_2^3 + \frac{1}{2}R_2^4 \right]$$

for HCl :

$$k_0 = -\frac{2e^2}{r_0^3} + \frac{e^2}{r_0^3} e^{-R_3} \left[16 + 16R_3 + 8R_3^2 + 3R_3^3 - \frac{1}{2}R_3^4 + (3/2)R_3^5 - (19/36)R_3^6 + (5/72)R_3^7 \right]$$

for HBr :

$$k_0 = -\frac{2\varepsilon^2}{r_0^3} + \frac{\varepsilon^2}{r_0^3} e^{-R_4} \left[16 + 16R_4 + 8R_4^2 + 3R_4^3 - R_4^4 + (31/10)R_4^5 \right. \\ \left. - (191/90)R_4^6 + (491/720)R_4^7 - (17/180)R_4^8 + (7/1440)R_4^9 \right]$$

for HI :

$$k_0 = -\frac{2\varepsilon^2}{r_0^3} + \frac{\varepsilon^2}{r_0^3} \cdot \frac{e^{-R_5}}{7200} \left[115200 + 115200R_5 + 57600R_5^2 + 21600R_5^3 \right. \\ \left. - 10800R_5^4 + 286560R_5^5 - 204040R_5^6 + 40280R_5^7 - 5210R_5^8 \right. \\ \left. + 742R_5^9 - 53R_5^{10} + (3/2)R_5^{11} \right]$$

Knowing R_n and r_0 for the different halides, we can determine the corresponding k_0 and thus ω_0 .

The experimental data, taken from Herzberg³¹ have been tabulated in Table I. The ionic energy D_1 has been calculated by the equation :

$$D_1 = D_0 + I(H) - E(X)$$

where D_0 is the Dissociation energy, $I(H)$ is the ionization potential of Hydrogen and $E(X)$ is the electron affinity of the halogen X. Electron affinities have been taken from Pritchard³².

Table II shows the calculated values of ω_0 and D_1 .

TABLE I—Observed values

HX	ω_0 cm ⁻¹	r_0 A	D_0 e. v.	D_1 e. v.
HF	4138.5	0.9171	6.66	16.63
HCl	2989.7	1.275	4.62	14.38
HBr	2649.7	1.414	3.914	13.96
HI	2309.5	1.604	3.196	13.55

TABLE II—Calculated values

HX	R_n	ω_0 cm ⁻¹	D_1 10 ⁻¹² ergs	D_1 e. v.
HF	7.94	4820	21.28	13.28
HCl	12.0	3370	15.89	9.92
HBr	15.95	3130	14.62	9.13
HI	20.44	3080	13.21	8.24

DISCUSSION

It will be observed that for all the four halides, the calculated α_0 is higher and D_1 lower than the observed ones. However, this is not surprising, because we assumed a completely ionic model for these molecules, which is not true. The covalent structure is also known to make sufficient contribution. The percentage difference between the observed and the calculated D_1 increases as we pass from HF to HI, which obviously indicates the lessening influence of the ionic structure. This is in agreement with finding from other view points, that the ionic structure decreases from HF to HI.

Similar results, i. e. low calculated D_1 have been found by other workers, who have assumed ionic models (e. g. Kirkood¹³, Gáspár and Kónya²¹, Horvath¹⁷, Náráy²⁰).

The fact that we have been able to calculate the ionic binding energy, enables us to calculate an important parameter regarding the structure of hydrogen halides, viz. the "fractional ionic character."

Wall² took the wave function (unnormalized) for the molecule as

$$\psi = \psi_0 + \lambda \psi_1$$

where ψ_0 is a purely covalent function and ψ_1 a purely ionic function, and λ is a parameter. To get the best energy value from this function, he minimized the energy expression with respect to λ . If W represents the minimized value and W_0 and W_1 the covalent and ionic energies, then he showed that :

$$\lambda^2 = \frac{W_0 - W}{W_1 - W}$$

Following Pauling and Sherman²³, Wall assumed

$$W_0(\text{HX}) = [W(\text{H}_2) W(\text{X}_2)]^{\frac{1}{2}}$$

and estimated W_1 by an electrostatic model with inverse power repulsion term. Thus λ^2 could be calculated.

In our notation :

$$W = -D_0$$

$$W_1 = - [D_1 - I(\text{H}) + E(\text{X})]$$

Further the fractional ionic character f is given by :

$$f = \frac{\lambda^2}{1 + \lambda^2}$$

For our case, we give in Table III the various calculated quantities.

TABLE III

	W	W_0	W_1	λ^2	f
HF	-6.66	-3.65	-3.31	.899	.473
HCl	-4.62	-3.45	-1.155	.262	.208
HBr	-3.914	-3.07	+.92	.175	.149
HI	-3.196	-2.72	+2.11	.075	.070

Fractional ionic characters (or λ^2) for these molecules have been calculated by several workers by different methods.

Table IV summarizes their results along with ours.

TABLE IV—*Fractional ionic character*

Author	HF	HCl	HBr	HI
Pauling ⁷ (1940)	(.60)	.17	.11	.05
Clark ³⁴ (1936)	.383	.175	.119	.053
Wall ² (Second set)	.303	.134	.107	.063
Davies ⁵	.68	.62	.60	.56
Robinson ³²		.565		
Coulson ³⁵	.43	.17	.11	.05
Schatz ²⁷		.547		
Varshni	.473	.208	.149	.070

The main point of dispute between the various workers is regarding the variation of 'f' as we pass from HF to HI. While Pauling⁷, Clark³⁴ and Coulson's³⁵ results show a very sharp decrease, those of Davies⁵ indicate only a slight decrease. Our results, calculated by very different methods than those of Pauling, Clark and Coulson (who calculated it from dipole moments) show a striking resemblance to their results. It appears rather unlikely that it is only fortuitous.

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ON THE MOMENTS OF MULTIVARIATE

MULTINOMIAL DISTRIBUTION

By

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1. Wishart (1949) has found the cumulants of multivariate multinomial Distributions. Here I shall find the moments of multivariate Multinomial Distribution.

Let p_1, p_2, p_n be the probability of happening of an event in any of n ways having p_0 as the chance of failure, then in case of multinomial distribution the probability of x_1 successes of the first kind x_2 of the second kind and x_n of the last out of S trials is

$$\frac{S!}{x_0! x_1! \dots x_n!} p_0^{x_0} p_1^{x_1} \dots p_n^{x_n}$$

Then the probability generating function $\varphi(t_1, t_2, \dots, t_n)$ has been given by Wishart (1949) as

$$a_0^{-S} [1 + \sum_{i=1}^n a_i e^{t_i}]^S$$

$$\text{where } \frac{p_i}{p_0} = a_i \ (i=1, 2, \dots, n) \text{ and } a_0 = 1 + \sum_{i=1}^n a_i$$

$$\frac{\partial \phi}{\partial t_1} = [S a_1 e^{t_1} a_0^{-S} [1 + \sum_{i=1}^n a_i e^{t_i}]^{S-1}]$$

$$\frac{\partial \phi}{\partial a_1} = a_0^{-S} S e^{t_1} [a_0 + \sum_{i=1}^n a_i e^{t_i}]^{S-1} - S a_0^{-(S+1)} [a_0 + \sum_{i=1}^n a_i e^{t_i}]^S$$

$$\frac{\partial \phi}{\partial t_1} = a_1 \frac{\partial \phi}{\partial a_1} + p_1 S \phi$$

$$\mu_1 \dots \mu_r \dots \mu_n = \left(\frac{\partial \phi}{\partial t_1} \right)_{t_i=0} = S \frac{a_1}{a_0} = S p_1$$

$$\mu_1 r \dots r_1 + 1 \dots r_n = \left[a_1 \frac{\partial}{\partial a_1} + p_1 \right] \mu_{r_1 \dots r_1 \dots r_n}$$

$$\mu_r + 1 = a_0 \frac{\partial \mu_r}{\partial a_1} + p_1 \mu_r \ (r \geq 1)$$

$$= p q \frac{\partial \mu_r}{\partial p} + p \mu_r$$

$$\text{Since } a_1 \frac{\partial p_1}{\partial a_1} = -a_1 \frac{\partial q_1}{\partial a_1} = p_1 q_1 \text{ where } q = 1 - \phi_1$$

$$a_j \frac{\partial p_1}{\partial a_j} = -a_j \frac{\partial q_1}{\partial a_j} = -p_1 p_j \ (i \neq j)$$

We have the moments upto third order

$$\mu \dots 1 = sp_1$$

$$\mu \dots 2 \dots = sp_1 q_1 + s^2 p_1^2 \quad \mu \dots 11 \dots = s(s-1) p_1 p_1$$

$$\mu \dots 21 \dots = s(s-1) p_1 p_1 (q_1 - p_1) + s^2 (s-1) p_1^2 p_1$$

$$\mu \dots 111 = s(s-1) (s-2) p_1 p_1 p_1$$

$$\mu_{r_1+1} r_2+1 \dots r_n+1 = \prod_{i=1}^n \left[a_i \frac{\partial}{\partial a_i} + sp_i \right] s(s-1) \dots (s-n+1) \times p_1 p_2 \dots p_n.$$

The probability in Pascalmultinomial distribution i. e. the multinomial generalisation of negative binomial is given by

$$\frac{(s-1+\sum x_i)!}{(s-1)! x_1! \dots x_n!} p_0^s p_1^{x_1} \dots p_n^{x_n}$$

The probability function $\phi(t_1 \dots t_n)$

$$= p_0^s \left[1 - \sum_{i=1}^n p_i e^{t_i} \right]^{-s} \text{ where } p_0 = 1 - \sum_{i=1}^n p_i$$

$$\frac{\partial \phi}{\partial t_1} = sp_0^s p_1 e^{t_1} \left[1 - \sum_{i=1}^n p_i e^{t_i} \right]^{-s-1}$$

$$\frac{\partial \phi}{\partial p_1} = sp_0^s e^{t_1} \left[1 - \sum_{i=1}^n p_i e^{t_i} \right]^{-s-1}$$

$$= sp_0^{s-1} \left[1 - \sum_{i=1}^n p_i e^{t_i} \right]^{-s}$$

$$\frac{\partial \phi}{\partial t_1} = p_1 \frac{\partial \phi}{\partial p_1} + s \frac{p_1}{p_0} \phi$$

$$\mu \dots 1 \dots = s \frac{p_1}{p_0} = sa_1$$

$$\mu \dots 2 \dots = \left(p_1 \frac{\partial}{\partial p_1} + s \frac{p_1}{p_0} \right) \mu \dots 1 \dots$$

$$\mu_{r+1} = p \frac{\partial \mu_r}{\partial p} + s \frac{p}{q} \mu_r$$

$$\mu_{r_1, r_1+1 \dots r_n} = \left(p_1 \frac{\partial}{\partial p_1} + sa_1 \right) \mu_{r_1, r_1 \dots r_n}$$

then using the formulae

$$p_1 \frac{\partial a_1}{\partial p_1} = p_1 \frac{\partial b_1}{\partial p_1} = a_1 b_1$$

$$p_j \frac{\partial a_1}{\partial p_j} = p_j \frac{\partial b_1}{\partial p_j} = a_1 \times a_j \quad (i \neq j) \text{ where } b_1 = a_1 + 1$$

$$s \dots 1 \dots = s a_1 b_1 + s^2 a_1^2$$

$$\mu \dots 11 \dots = s(s+1) a_1 a_j$$

$$\mu \dots 3 \dots = s(a_1 b_1^2 + a_1^2 b_1) + s^2 a_1^2 (b_1 + s a_1)$$

$$\mu \dots 21 \dots = s(s+1) a_j a_1 b_1 + s(s+1) a_j^2 a_j + s(s+1) a_1^2 a_j$$

$$\mu \dots 111 \dots = s(s+1)(s+2) a_1 a_j a_k$$

3. Let there be variates which are the number of successes in two events. The respective probabilities are given as follows :—

1st event	2nd event		Total
	Success	Failure	
Success	P_{11}	P_{10}	p
Failure	P_{01}	P_{00}	q
	p'	q'	1

where $q=1-p$, $q'=1-p'$ and $p_{00}=1-p_{10}-p_{01}-p_{11}$

and $p_{00}p_{11}-p_{10}p_{01}=p_{11}-pp'$.

The frequency function for the probability of x_1 successes and $s-x_1$ failures in the first event and x_2 successes, $s-x_2$ failures in the second event is

$$f(x_1, x_2) = {}^s C_{x_1} \sum_{i=0}^{\min(x_1, x_2)} {}^{s-x_1} C_{x_2-i} p_{11}^i p_{01}^{x_2-i} p_{00}^{s-x_1-x_2+i} p_{10}^{x_1-i}$$

The probability generating function is

$$\phi(t, x) = a_{00}^{-s} (1 + a_{10} e^t + a_{01} e^u + a_{11} e^{t+u})^s$$

$$\text{where } a_{10} = \frac{p_{10}}{p_{00}}, a_{01} = \frac{p_{01}}{p_{00}}, a_{11} = \frac{p_{11}}{p_{00}}$$

$$a_{00} = 1 + a_{10} + a_{01} = p_{00}^{-1}$$

$$\frac{\partial \phi}{\partial t} = a_{00}^{-s} S(1 + a_{10} e^t + a_{01} e^u + a_{11} e^{t+u})^{s-1}$$

$$(a_{10} e^t + a_{11} e^{t+u})$$

$$\frac{\partial \phi}{\partial a_{11}} = S a_{00}^{-s} (1 + a_{10} e^t + a_{01} e^u + a_{11} e^{t+u})^{s-1} e^{t+u}$$

$$- S a_{00}^{-s-1} [1 + a_{10} e^t + a_{01} e^u + a_{11} e^{t+u}]^s$$

$$\frac{\partial \phi}{\partial a_{11}} = S a_{00}^{-s} [1 + a_{10} e^t + a_{01} e^u + a_{11} e^{t+u}]^{s-1} e^{t+u}$$

$$- S a_{00}^{-s-1} [1 + a_{10} e^t + a_{01} e^u + a_{11} e^{t+u}]^s$$

$$\frac{\partial \phi}{\partial t} = a_{10} \frac{\partial \phi}{\partial a_{10}} + a_{11} \frac{\partial \phi}{\partial a_{11}} + S \left(\frac{a_{10} + a_{11}}{a_{00}} \right) \phi.$$

$$\mu_{r_1 + 1, r_2} = \left(a_{10} \frac{\partial}{\partial a_{10}} + a_{11} \frac{\partial}{\partial a_{11}} \right) \mu_{r_1, r_2} + sp \mu_{r_1, r_2}$$

$$\mu_{r_1, r_2 + 1} = \left(a_{11} \frac{\partial}{\partial a_{11}} + a_{01} \frac{\partial}{\partial a_{01}} \right) \mu_{r_1, r_2} + ps \mu_{r_1, r_2}$$

$$\mu_{10} = Sp, \mu_{01} = Sp'$$

$$\text{Let } D = a_{10} \frac{\partial}{\partial a_{10}} + a_{11} \frac{\partial}{\partial a_{11}}, D' = a_{11} \frac{\partial}{\partial a_{11}} + a_{01} \frac{\partial}{\partial a_{01}}$$

$$D(p) = -D(q) = pq, D'(p') = -D'(q') = p'q'$$

$$D(p') = D'(p) = -D(q) = -D'(q) = p_{11} - pp'$$

$$D(p_{11} - pp') = (q - p) p_{(11)}, D'(p_{11} - pp') = (q' - p') p_{(11)}$$

$$\text{where } p_{(11)} = p_{11} - pp$$

Hence the moments upto third order

$$\mu_{10} = Sp$$

$$\mu_{01} = Sp'$$

$$\mu_{20} = Spq + S^2 p^2$$

$$\mu_{02} = Sp'q' + S^2 p'^2$$

$$\mu_{30} = Spq(q-p) + 2S^2 pq$$

$$\mu_{03} = Sp'q'(q'-p') + 2S^2 p'q'$$

$$+ Sp(Sp'q + S^2 p^2)$$

$$+ Sp'(Sp'q' + S^2 p'^2)$$

$$\mu_{111} = S(S-1)pp' + Sp_{11}$$

$$\mu_{21} = S^2 [pp'q + pp_{(11)}]$$

$$= S^2 pp' + Sp_{(11)}$$

$$+ S(q-p)p_{(11)}$$

$$\mu_{12} = S^2 [pp'q' + p'p_{(11)}]$$

$$+ S(q' - p')p_{(11)}$$

4. The probability function corresponding to bivariate Negative Binomial or Pascal Distribution is

$$\phi(t, u) = p_{00}^s [1 - p_{10}e^t - p_{01}e^u - p_{11}e^{t+u}]^{-s}$$

$$\text{where } p_{00} = 1 - p_{10} - p_{01} - p_{11}$$

$$\frac{\partial \phi}{\partial t} = sp_{00}^s [1 - p_{10}e^t - p_{01}e^u - p_{11}e^{t+u}]^{s-1}$$

$$(p_{10}e^t + p_{11}e^{t+u})$$

$$\frac{\partial \phi}{\partial p_{10}} = Sp_{00}^s [1 - p_{10}e^t - p_{01}e^u - p_{11}e^{t+u}]^{s-1} e^t$$

$$- Sp_{00}^{s-1} [1 - p_{10}e^t - p_{01}e^u - p_{11}e^{t+u}]^{-s}$$

$$\frac{\partial \phi}{\partial p_{11}} = Sp_{00}^s [1 - p_{10}e^t - p_{01}e^u - p_{11}e^{t+u}]^{s-1} e^{t+u}$$

$$- Sp_{00}^{s-1} [1 - p_{10}e^t - p_{01}e^u - p_{11}e^{t+u}]^{-s}$$

$$\frac{\partial \phi}{\partial t} = \left(p_{10} \frac{\partial}{\partial p_{10}} + p_{11} \frac{\partial}{\partial p_{11}} \right) \phi + s \left(\frac{p_{10} + p_{11}}{p_{00}} \phi \right)$$

$$\mu_{r_1 + 1, r_2} = \left(p_{01} \frac{\partial}{\partial p_{01}} + p_{11} \frac{\partial}{\partial p_{11}} \right) \mu_{r_1, r_2} + S a \mu_{r_1, r_2}$$

$$\mu_{r_1, r_2+1} = \left(p_{01} \frac{\partial}{\partial p_{01}} + p_{11} \frac{\partial}{\partial p_{11}} \right) \mu_{r_1, r_2} + S a' \mu_{r_1, r_2}$$

$$\mu_{10} = S a, \mu_{01} = S b \text{ where } a = a_{10} + a_{11}, a' = a_{01} + a_{11}$$

$$b = 1 + a, b = 1 + a'$$

$$\text{Let } D = p_{10} \frac{\partial}{\partial p_{10}} + p_{11} \times \frac{\partial}{\partial p_{11}}, D' = p_{11} \frac{\partial}{\partial p_{11}} + p_{10} \frac{\partial}{\partial p_{01}}$$

$$D(a) = D(b) = ab, D'(a') = D'(b') = a'b'$$

$$D(a') = D(b') = D'(a) = D'(b) = a_{11} + aa' = a_{(11)} \text{ say}$$

$$D[a_{(11)}] = (b+a) a_{(11)}, D'[a_{(11)}] = (b'+a') a_{(11)}$$

The table for moments upto 3 order

$$\mu_{10} = S a, \mu_{01} = S b, S_{20} = S a b + S^2 a^2$$

$$\mu_{02} = S a' b' + S^2 a, \mu_{30} = S a b (a+b) + 2 S^2 a b + S^2 a^2 b + S^2 a^2$$

$$\mu_{03} = S' a' b' (a' + b) + 2 S^2 a' b' + S^2 a'^2 b' + S^2 a'^3$$

$$\mu_{11} = [S a_{11} + a a'] + S^2 a a'$$

$$\mu_{21} = S(b+a) (a_{11} + a a') + S^2 a (a_{11} + a a') + S^2 a a' b$$

$$\mu_{12} = S(b' + a') (a_{11} + a' \times a) + S^2 a' (a_{11} + a a') + S^2 a a' b'$$

Applying similar methods we can find moments for multivariate multinomial distribution.

Patterns and moments from $(4 \times 3 \times 2)$ table to the		Number of cases	Moment
third order			
1st order	1 ...	8C_1	$\mu_1 = Sp$
	\vdots		
2nd order	2 ...	6C_1	$\mu_2 = Spq + S^2p^2$
	\vdots		
	11 . } }	6C_2	$\mu_{11} = S(S-1)p_1p_2$ $\mu_{1,1} = S(S-1)pp' + Sp_{11}$
		7C_2	
3rd order	3 ...	6C_1	$\mu_3 = Spq(q-p)$ $+ 2S^2pq + S^2p^2$
	21 . } }	6C_1	$\mu_{21} = S(S-1)p_1p_2(q_1-p_1)$ $+ S^2(S-1)p_1^2p_2$
	2... } }		$\mu_{2,1} = S(q-p)(p_{11}-pp')$ $+ S(S-2)p(p'q + p_{11}-pp')$
	111 } }	6C_3	$\mu_{111} = S(S-1)(S-2)p_1p_2p_3$
		8C_3	

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DIFFRACTION OF OBLIQUE SHOCK WAVE PAST A SMALL BEND*

By

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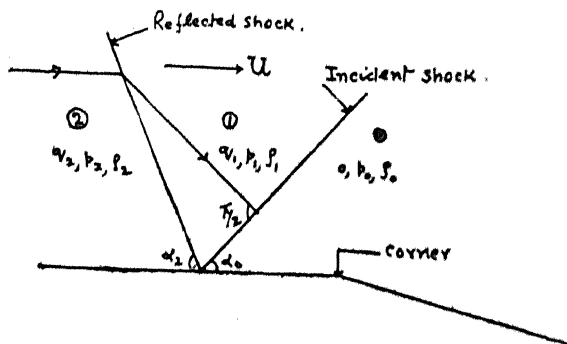
Read at the Silver Jubilee Session on 28th December 1955 at the University of Lucknow

(Communicated by Prof. P. L. Srivastava)

INTRODUCTION

Lighthill in the year 1949 investigated the encounter of a plane normal shock with a solid corner of small angle. He calculated the pressure rise across the shock wave and the shape of the bend after the shock front had crossed the corner. Here we shall take the case of an oblique shock wave and will prove mathematically that after the shock configuration has passed the corner, the region between the incident and reflected shocks will not be disturbed for all possible shock strengths.

Formulation of the Problem



In the figure the subscript (0) refers to the front side of the incident shock, the subscript (1) to the region between the incident and reflected shocks and the subscript (2) to the back side of the reflected shock. U is the shock velocity. The shock configuration is approaching the corner 0.

Since in region (0), the air is at rest, continuity of tangential component of momentum gives q_1 perpendicular to the incident shock front. Therefore from Lighthill's expressions we get for air (assumed to be polytropic with adiabatic index $\gamma=1.4$)

$$q_1 = \frac{5}{6} \bar{U} \left(1 - \frac{a_0^2}{U^2} \right), \quad p_1 = \frac{5}{6} p_0 \left(U^2 - \frac{a_0^2}{7} \right), \quad \rho_1 = \frac{6\rho_0}{1 + \frac{5a_0^2}{U^2}} \quad (1)$$

where $\bar{U} = U \sin \alpha_0$,

$$\text{and } \bar{q}_2 = \bar{q}_1 + \frac{5}{6} (U^* - \bar{q}_1) \left\{ 1 - \frac{a_1^2}{(U^* - \bar{q}_1)^2} \right\} \quad (2.1)$$

*The paper was also read at the first congress on theoretical and applied mechanics, Kharagpur with certain modifications.

$$p_2 = \frac{5}{6} \rho_1 \left\{ (U^* - q_1)^2 - \frac{a_1^2}{7} \right\} \quad (2.2)$$

$$\rho_2 = \frac{6\rho_1}{\left\{ 1 + \frac{5a_1^2}{(U^* - q_1)^2} \right\}}$$

where $U^* = U \sin \alpha_2$, $q_1 = -q_1 \cos(\alpha_0 + \alpha_2)$, and $q_2 = q_2 \sin \alpha_2$.

The equation in α_2 is

$$q_1 \cos \alpha_0 \sec^2 \alpha_2 - \frac{5}{6} [U \tan \alpha_2 + q_1 (\cos \alpha_0 - \tan \alpha_2 \sin \alpha_0)] \times \left[1 - \frac{a_1^2 \sec^2 \alpha_2}{\{U \tan \alpha_2 + q_1 \sec \alpha_2 \cos(\alpha_2 + \alpha_0)\}^2} \right] = 0 \quad \dots \quad (3)$$

In region (1), let \vec{Q}_2 , P_2 , σ_2 , S_2 be the velocity, pressure, density and entropy at any point. Choose (X, Y) axes with origin at the corner, X-axis along the original wall produced. If $\frac{D}{Dt} = \frac{\partial}{\partial t} + \vec{Q} \cdot \nabla$ signifies time rate of change for a given fluid element, the equations of conservation of mass and momentum can be written

$$\frac{D\sigma_2}{Dt} + \sigma_2 \operatorname{div} \vec{Q}_2 = 0, \quad \frac{DQ_2}{Dt} + \frac{1}{\sigma_2} \nabla P_2 = 0$$

and if there is no heat transfer between fluid elements by friction conduction or radiation the entropy will satisfy $\frac{DS_2}{Dt} = 0$

On the assumption that \vec{Q}_2 , P_2 , σ_2 differ only by small quantities from the values $\{q_1 \sin \alpha_2 (=u_1), -q_1 \cos \alpha_0 (=v_1)\}$, p_1 , ρ_1 which they had before diffraction, the equations of motion can be approximated as

$$\left. \begin{aligned} \frac{\partial \sigma_2}{\partial t} + u_1 \frac{\partial \sigma_2}{\partial X} + v_1 \frac{\partial \sigma_2}{\partial Y} + \rho_1 \operatorname{div} \vec{Q}_2 &= 0 \\ \frac{\partial Q_2}{\partial t} + u_1 \frac{\partial Q_2}{\partial X} + v_1 \frac{\partial Q_2}{\partial Y} + \frac{1}{\rho_1} \nabla P_2 &= 0 \\ \frac{\partial S_2}{\partial t} + u_1 \frac{\partial S_2}{\partial X} + v_1 \frac{\partial S_2}{\partial Y} &= 0 \end{aligned} \right\} \dots \dots \dots (4)$$

The entropy and density variations can now be eliminated from the entire problem, since by virtue of the last equation

$$\frac{\partial \sigma_2}{\partial t} + u_1 \frac{\partial \sigma_2}{\partial X} + v_1 \frac{\partial \sigma_2}{\partial Y}$$

can be replaced by

$$\left(\frac{\partial \rho_1}{\partial p_1}\right) \left(\frac{\partial P_2}{\partial t} + u_1 \frac{\partial P_2}{\partial X} + v_1 \frac{\partial P_2}{\partial Y}\right) = \frac{1}{a_1^2} \left(\frac{\partial P_2}{\partial t} + u_1 \frac{\partial P_2}{\partial X} + v_1 \frac{\partial P_2}{\partial Y}\right)$$

owing to the thermodynamic principle that the density is a function of pressure and of entropy alone.

Let us now make the transformations

$$\frac{X - u_1 t}{a_1 t} = x, \frac{Y - v_1 t}{a_1 t} = y, \vec{Q}_2 = \left\{ u_1 (1 + u), v_1 (1 + v) \right\}, \frac{P_2 - p_1}{a_1 \rho_1} = p$$

These reduce the first two equations of (4) to

$$x \frac{\partial p}{\partial x} + y \frac{\partial p}{\partial y} = u_1 \frac{\partial u}{\partial x} + v_1 \frac{\partial v}{\partial y}.$$

$$\left(x \frac{\partial u}{\partial x} + y \frac{\partial u}{\partial y} \right) u_1 = \frac{\partial p}{\partial x},$$

$$\left(x \frac{\partial v}{\partial x} + y \frac{\partial v}{\partial y} \right) v_1 = \frac{\partial p}{\partial y}.$$

Putting $uu_1 = \bar{u}$, $vv_1 = \bar{v}$, these become

$$x \frac{\partial p}{\partial x} + y \frac{\partial p}{\partial y} = \frac{\partial \bar{u}}{\partial x} + \frac{\partial \bar{v}}{\partial y}.$$

$$x \frac{\partial \bar{u}}{\partial x} + y \frac{\partial \bar{u}}{\partial y} = \frac{\partial p}{\partial x}.$$

$$x \frac{\partial \bar{v}}{\partial x} + y \frac{\partial \bar{v}}{\partial y} = \frac{\partial p}{\partial y}.$$

Eliminating \bar{u} , \bar{v} , the equation in p is

$$\nabla^2 p = \left(x \frac{\partial}{\partial x} + y \frac{\partial}{\partial y} + 1 \right) \left(x \frac{\partial p}{\partial x} + y \frac{\partial p}{\partial y} \right).$$

This is hyperbolic for $x^2 + y^2 > 1$ and elliptic for $x^2 + y^2 < 1$; its characteristics are all tangents to the unit circle $x^2 + y^2 = 1$.

We may therefore assume that the smallest region of non-uniform flow in (1) is bounded by an arc of the circle $x^2 + y^2 = 1$, the two shocks and the wall. If such a region exists, the point P where the two shocks join must lie within the unit circle.

As a first approximation, the position of P is given by $X = Ut$, $Y = 0$, i.e.,

$$x = \frac{U - u_1}{a_1}, \quad y = -\frac{v_1}{a_1}.$$

P therefore lies inside the unit circle if

$$\left(\frac{U - u_1}{a_1} \right)^2 + \frac{v_1^2}{a_1^2} < 1,$$

i.e. if $U^2 - 2U q_1 \sin \alpha_0 + q_1^2 < a_1^2$

Substituting for q_1 and a_1 from equations (1), we see that (5) is satisfied if

$$7\bar{U}^4 - 2\bar{U}^2 (3U^2 - 2a_0^2) - 5a_0^4 > 0.$$

For this to be true, \bar{U}^2 must not lie between the roots of the equation

$$7x^2 - 2x (3U^2 - 2a_0^2) - 5a_0^4 = 0.$$

One root of this equation is negative. Hence region (1) will be disturbed if

$$7\bar{U}^2 > 3U^2 - 2a_0^2 + \sqrt{(3U^2 - 2a_0^2)^2 + 35a_0^4}$$

That is, if

$$7 \sin^2 \alpha_0 > 3 - \frac{2}{M^2} + \frac{\sqrt{(3U^2 - 2a_0^2)^2 + 35a_0^4}}{U^2}$$

where M is the Mach number $\frac{U}{a_0}$.

Now, from Rankine-Hugoniot equations we have

$$\frac{p_1}{p_0} - 1 = \frac{2\gamma}{\gamma+1} (M^2 \sin^2 \alpha_0 - 1).$$

Putting $\gamma = 1.4$ and $\xi = \frac{p_0}{p_1}$, this gives

$$\frac{1}{M^2} = 7 \sin^2 \alpha_0 \frac{\xi}{\xi + 6}$$

Substituting this value of $\frac{1}{M^2}$ in inequality (6) and simplifying we find that for flow in region (1) to be disturbed

$$\sin^2 \alpha_0 > \frac{\{\xi + 6\}^2}{7(6 + 6\xi - 5\xi^2)}.$$

Or in other words the region (1) will or will not be disturbed according as

$$\alpha_0 > \text{ or } < \alpha_0^*$$

$$\text{where } \sin^2 \alpha_0^* = \frac{(\xi + 6)^2}{7(6 + 6\xi - 5\xi^2)} \quad \dots(7)$$

We shall now show that α_0^* is greater than the extreme value of the angle of incidence consistent with regular reflection of the incident shock.

From Bleakney and Taub's paper (1949), we obtain x' as

$$x' = \frac{-x(1 + \eta^2 x^2) \pm \sqrt{x^2(1 + \eta^2 x^2)^2 - (1 + \eta x^2)\{(\gamma + 1)(\eta - 1) + 2\}}}{(1 + \eta x^2)[(\gamma + 1)(\eta - 1) + 2]} \times \frac{(\eta - 1)\{(\gamma - 1)(1 + \eta x^2) + 2\}}{\dots(8)}$$

Where $x = \tan \tau = \cot \alpha$ (as $\tau = \frac{\pi}{2} - \alpha$) (α being angle of incidence).

$$x' = \tan \tau \text{ and } \eta = \frac{(\gamma + 1) + (\gamma - 1)\xi}{(\gamma - 1) + (\gamma + 1)\xi}$$

Now the value of x' becomes complex when

$$x^2 (1 + \eta^2 x^2)^2 < (1 + \eta x^2) (\eta - 1) \{ (\gamma + 1) (\eta - 1) + 2 \} \\ \times \{ (\gamma - 1) (1 + \eta x^2) + 2 \} \dots \dots \dots (9)$$

When (9) holds, Mach reflection takes place. When the inequality sign in (9) is replaced by an equality sign we obtain an expression for the extreme value $\alpha_{ext.}$ of the angle of incidence.

Hence the expression for $\alpha_{ext.}$ is

$$x^2 (1 + \eta^2 x^2)^2 = (1 + \eta x^2) (\eta - 1) \{ (\gamma + 1) (\eta - 1) + 2 \} \\ \times \{ (\gamma - 1) (1 + \eta x^2) + 2 \} \dots \dots \dots (10)$$

where $x = \cot \alpha_{ext.}$

$$\text{Now } \eta = \frac{(\gamma + 1) + (\gamma - 1) \xi}{(\gamma - 1) + (\gamma + 1) \xi} = \frac{6 + \xi}{1 + 6\xi}$$

Since γ has been taken equal to 1.4.

Also we note from this that when $(0 \leq \xi \leq 1)$ we have $(1 \leq \eta \leq 6)$

In (10), putting $\gamma = 1.4$ and simplifying we get

$$25 \eta^4 x^6 + x^4 \eta^2 \{ 50 - 4 (\eta - 1) (6\eta - 1) \} \\ + x^2 \{ 25 - 28\eta (\eta - 1) (6\eta - 1) \} \\ - 24 (\eta - 1) (6\eta - 1) = 0 \dots \dots \dots (11)$$

Now (11) can be written in the form

$$25t (z^2 t + 1)^2 = 4 (z - 1) (6z - 1) (zt + 1) (zt + 6) \dots \dots \dots (12)$$

where $t = x^2$ and $\eta = z$

$$\text{From (7) we get } \cot^2 \alpha_0^* = \frac{6}{5} \frac{(\eta - 1)}{\eta^2} = \frac{6}{5} \frac{(z - 1)}{z^2} \text{ as } \eta = z. \dots \dots \dots (13)$$

Now if we regard t as independent variable and z as dependent we can plot a graph ($\cot^2 \alpha_0^*$ versus η) from (13) and another ($\cot^2 \alpha_{ext.}$ versus η) from (12). Solving (12) and (13) we get the points of intersections of the two curves as

$$z = \frac{29}{44}$$

$$z = \frac{1}{6}$$

$$z = \infty$$

$$\text{and } z = 1$$

The first three values are inadmissible as $1 \leq z \leq 6$. The two curves therefore intersect only at the point given by $z = 1$. From (12) and (13) it is clear that when $z = 1$, $t = 0$

$$\text{i.e., } a_{\text{ext.}} = a_0^* = \frac{\pi}{2}$$

For the curve (12)

$$\left(\frac{dt}{dz}\right)_{z=1} = 4.8.$$

and for the curve (13)

$$\left(\frac{dt}{dz}\right)_{z=1} = 1.2$$

Therefore $\left(\frac{dt}{dz}\right)_{z=1}$ for the curve represented by (12) is greater than $\left(\frac{dt}{dz}\right)_{z=1}$ for the curve represented by (13).

It is easy to see that the two curves given by (12) and (13) represent continuous functions for $1 \leq z \leq 6$.

We therefore conclude that the curve given by (12) i.e. ($\cot^2 \alpha_{\text{ext.}}$ versus η) remains always above the curve ($\cot^2 \alpha_0^*$ versus η) for ($1 \leq z \leq 6$).

We now know that $\cot \theta$ decreases as θ increases ($0 \leq \theta \leq \pi_2$) the natural consequence of the above result will therefore be that the curve (α_0^* versus η) always remains above the curve ($\alpha_{\text{ext.}}$ versus η).

Consequently for every admissible value of η (or ξ) i.e. for all possible shock strengths we shall always have

$$\alpha_0^* > \alpha_{\text{ext.}}$$

Hence the region (1) i.e. the region between the reflected shock and the incident shock will not be disturbed for all possible shock strengths.

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ON PIEZOELECTRIC INVESTIGATION OF CRYSTAL FRAGMENTS

By

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Communicated by Prof. K. Banerjee

(Read at the Annual Session on 29th December 1954)

Various methods have already been tried for testing the presence of piezoelectric effect in substances and different sensitivities have been achieved. In this paper has been presented a short account of the method that is being used in this laboratory for measurements on small crystal fragments (1 to 2 mm. cubes) and which, it is considered, would be especially suitable for very weakly piezoelectric crystals.

The electrical behaviour of a piezoelectric crystal^{8,9,10,11} can be represented with good approximation near a resonant frequency, assuming a simple mode of vibration, by the equivalent circuit of fig (1). The impedance of the crystal

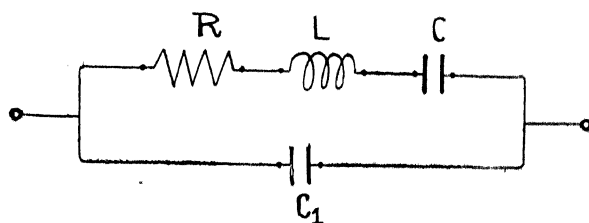


Fig (1)

undergoes a minimum and a maximum at the resonant and the antiresonant frequencies, given by

$$\left. \begin{aligned} f_r &= f_0 - \frac{1}{2}f_0 \left[\frac{1}{Q_0^2} \cdot \left(\frac{C_1}{C} \right) \right] \\ f_a &= f_0 + \frac{1}{2}f_0 \left[\frac{C}{C_1} + \frac{1}{Q_0^2} \cdot \left(\frac{C_1}{C} \right) \right] \end{aligned} \right\} \dots \dots (1)$$

$$\left. \begin{aligned} \text{where } f_0 &= \frac{1}{2\pi \sqrt{LC}} \\ \text{and } Q_0 &= \frac{1}{2\pi f_0 RC} \end{aligned} \right\} \dots \dots \dots (2)$$

On neglecting $\left(\frac{1}{Q_0^2} \right)$, these reduce to

$$\begin{aligned} f_r &\approx f_0 \\ f_a &\approx f_0 + \frac{1}{2}f_0 \left(\frac{C}{C_1} \right) \end{aligned}$$

Consequently the ratio of $\left(\frac{C}{C_1}\right)$, which would in a sense be a measure of the piezoelectric effect, can be determined by means of the relation

$$\left(\frac{C}{C_1}\right) = 2 \frac{f_a - f_r}{f_r} \quad \dots \quad \dots \quad \dots \quad (3)$$

The effective coupling coefficient^{11,12}, k' , for crystal fragments, whose geometrical form factor, G , is not known, can be determined by the approximate relation

$$k' = \frac{k}{G} = \frac{\pi}{2} \left(\frac{f_a - f_r}{f_r} \right)^{\frac{1}{2}}$$

When therefore the applied signal across a piezoelectric crystal is varied in frequency, the abrupt change in the dynamic impedance of the crystal, as it passes the resonant frequency, brings about changes in the voltage and current relationships. These changes can be made noticeable from three different approaches. In the first place the impedance change can be detected by an impedance measuring device such as the disbalancing of an appropriate impedance bridge¹². In the second place this crystal impedance can be reflected into an oscillator circuit and an abrupt change of this impedance can be made responsible for an amplitude (and/or frequency) change of the oscillator output^{1,3,4,5,6,7}. This results into an amplitude modulation of the radio-frequency carrier and produces a 'click' on demodulation. In the third place as the crystal begins to vibrate at the resonant frequency, and because of the higher value of Q_0 , the crystal continues to vibrate for a certain time depending upon circuit characteristics, while the applied signal has changed its frequency. This superposition of two voltages, one of constant amplitude and varying frequency and the other of constant frequency but a varying amplitude, results in a decaying varying-pitch audio beat which can be detected².

The output curve from the bridge method resembles the single-peaked resonance curve which, however, yields information only of the motional constants of the crystal, R , L , and C . It does not give any information about the shunt 'clamped-crystal' capacitance, C_1 . The width of the resonant curve gives the motional Q_0 of the crystal:

$$Q_0 = \frac{f_0}{f_1 - f_2}$$

Where f_1 and f_2 are the frequencies of the -707 points and f_0 the frequency for maximum output. The motional resistance, R , is determined from the height of the curve at f_0 . L and C can then be obtained from the relations (2). The sensitivity of this method is due to the fact that it is a differential method and the full sensitivity of the detector is made use of.

The sensitivity of the method employing the impedance-reflection depends upon the circuit characteristics. This method, however, does not give accurately the electrical constants of the crystal, but serves very well the purpose of a piezoelectric detector, only indicating the presence of piezoelectricity in crystals. Nevertheless, just the presence of piezoelectricity in substances is a valuable information to

crystallographers. The method that is being used in this laboratory is based on this principle. In fig. (2) has been shown a somewhat simplified circuit diagram of the apparatus. The crystal fragments placed in an especially made holder

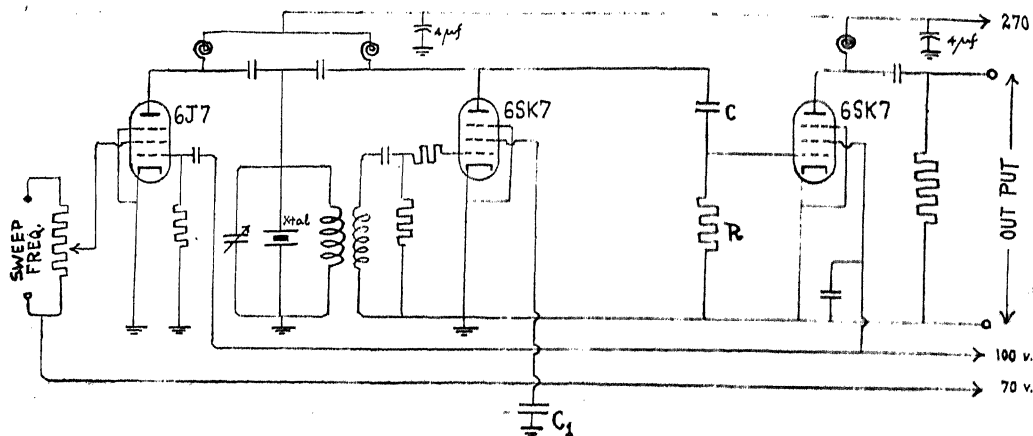


Fig 2

is placed in parallel to the tank circuit of an oscillator. Any change of impedance of the tank circuit will disturb the Barkhausen's conditions of oscillation, so that the self-maintained grid bias of the oscillator tube would shift to a value to give a corresponding transconductance, g_m , such that the Barkhausen's conditions are restored. This results into a change of the amplitude of oscillations, which in turn is equivalent to an amplitude modulation of the radio-frequency carrier. The output from the apparatus is amplified and viewed on an oscillograph screen. The frequency of the oscillator is varied manually while it is being constantly wobbled (electronically). The presence of piezoelectricity will be thrown on the oscillograph screen as an audio-frequency noise. As a means of increasing the sensitivity a variable- μ pentode having a high value of plate resistance and a more or less exponential g_m - e_g curve has been selected as the oscillator tube. The use of a separate detector tube, employing another super-control pentode used as an anode-detector and proper choice of the grid-leak grid-capacitor combination further increases the sensitivity. A sharp cut-off pentode with high plate resistance, low screen and plate currents and a linear g_m - e_g curve has been used as the frequency wobbulator. The variation of g_m of the wobbulator tube with its screen volts is also linear. As a means to check unforeseen resonances and generation of violent self-maintained frequency modulation, the coupling impedance between the oscillator and the grid of the wobbulator tube, C_1 in fig (2) (which is responsible for making the latter act as a reactance valve), has been decoupled from the tank circuit; and an electronic coupling is used instead through the screen grid of the oscillator pentode. The oscillator tube has been especially chosen to have a value of the screen current which should suffice for the appropriate coupling impedance. The bandwidth of wobblelation has been kept large on grounds of ease of operation. The sweep frequency of the oscillograph is fed to the wobbulator.

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THE SOILS OF WEST BENGAL PART II (NADIA)¹

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The district of Nadia is situated in the centre of the Gangetic West Bengal, on the eastern flank of the Bhagirathi, within the parallels of 22°53' and 24°11' north latitude and 88°09' and 88°48' east longitude.

The landscape is, an alluvial plane, dotted with villages surrounded by clusters of groves, intersected by numerous small rivers, abandoned river courses, minor streams, swamps and lakes. The maximum recorded height above sea level is 56 ft. on the north and the minimum is 24 ft. in the south, the inclination of slope is towards the south east. Saucer shaped depressions occur in many areas.

The Bhagirathi entering the district on the north follow a meandering course and together with its numerous tributaries, mainly Jalangi and Churni drain the area. On both sides of these three rivers there are either high ridges or flood basins. The flood basins get submerged by the river floods during monsoons. During flood, the banks of rivers are subjected to severe impacts, which result in swinging the river to the right or left in its course and often the river bed gets so much choked up by the deposition of sand and silt that the rivers abandon their course and force their way through new channels. The lower part of Bhagirathi i.e. the portion lying south of Nabadwip is subject to the daily rise of water table due to tides. Thus this district presents soils which have been in the one hand deposited by the rivers, which have undergone subsequent weathering and leaching due to humidity, high temperature and rainfall and in the other hand formed by the processes leading to the maximum clay deposition due to tidal action on account of tidal water rushing into lower reaches of the Bhagirathi.

A common feature which one observes during field studies, is an occurrence of an unending series of blister like soil moulds, covering up in irregular successions in fallow or wastelands. These are similar to those observed by Whitehouse² at Queensland. This is a very important soil forming process active in this region.

Schematic type of soil survey was adopted³. The profiles were studied at 6 mile intervals from representative cultivated areas up to a depth of 4 ft.⁴ The scheme and methods of analysis followed were as given in Sigmond⁵, A.E.A.⁶ Williams⁷ and Wright⁸.

-
1. The soil-work was taken up at the initiative of Sri K. Sen, I.C.S.
 2. Tropical soils by Mohr & Barren (1954) pp 360.
 3. Soil Survey Manual No. 18. U. S. D. A. (1951) pp. 15-21 etc.
 4. Ibid pp. 171.
 5. The principals of soil science by De Sigmond 1938 pp. 84-116.
 6. A. E. A. 1931.
 7. Williams, R. J. Agri. Sci. 18, 439, (1928)
 8. Wright, C. H. methods of soil analysis. Thomas Murby & Co., London 1939,

METEOROLOGICAL DATA

Average rainfall of the District	60.06 inches
Number of rainy days	81.4 days
Rainy months above 5" of rainfall p.m.	July to October
Average relative humidity Mean of 8 hrs.	75.06
Mean of 17 hrs.	59.54
Average temperature	79.4°F
Langs factor	58.0
Meyers N-S-Q	227.9

CROPS

Paddy, (Aus & Aman) Sugarcane, Jute and Pulses are the principal food and cash crops. The acreage under each of these crops are given below (in thousand acres).

Aus	=254.5	Aman	=	218.4
Sugarcane	= 5.0	Jute	=	45.0
Pulses &				
Oilseeds	=159.7			

Aus - pulses - Aus or Jute - pulses - Jute are the common rotations.

Mango & Jackfruits grow well & bear plentifully. Orchard growing is a profitable land use in the area.

SOILS

Langs factor is suggestive of formation of Brown earthgroup¹ of soils and Meyers Quotient of chestnut - brown - steppe² soils and degraded chernozems.

The following are the natural soil regions formed as a result of the physical features, watershed and the climate. The parent material is Ganga Alluvium, which under different soil forming factors have led to the formation of three soil series. They are :

- (1) Ganga Riverine lands
- (2) Ganga Flat lands
- (3) Ganga Low Lands

The series Ganga Riverine Lands has two phases. They are :

- (a) Inundated phase : Ganga Riverine Char Lands.
- (b) High land phase : Ganga Riverine Ridges.

1. Jenny, H. Soil Research 1, 183. (1929).

2. Ibid.

GANGA RIVERINE LANDS

These are formed of soils on recent alluvial fans, flood-plains, or other secondary deposits, having undeveloped profiles and underlain by unconsolidated material. These profiles show no accumulation of clay or lime in the sub-soil resulting from weathering and the downward movement of water from surface horizon. Deposition of alluvium having different texture in different layers in an unsystematic manner is evident. The soils of this series examined occur in the Police Stations of :

Karimpore—In the portion bounded by the road from the ferry at Narayanpur, to the P. S. Karimpur and the Jalangi.

Tehatta—(a) The portion lying west and north-west of the road from the Post Office Betai to Tehatta and West of the road from Tehatta to the G. T. S. at Palasipara. (b) The area between the Bhairab and its tributary on the left bank.

Plassey—The part on the north of the road from Bhaga to Kaliganj.

Nakashipara—(a) West of the road running from Khajuri, via Muragachcha G. T. S. and Gotpara to Bhaga. (b) East of the road from Khajuri to Patkiabari via R. S. Bethuadauri.

Krishnagar—The entire area except the portion lying between the roads to Hanskhali and to Krishnaganj.

Chapra—In the south eastern part.

Hanskhali—The portion lying in the area south of the road to Hanskhali from Krishnagar and east of the Churni.

Santipore—The entire Police Station.

Ranaghat—(a) Via Nilnagar in the south west of the road from Chakdah to Ranaghat, except the portion on the east of Nilnagar and G. T. S. Paschim Noapara and the north of the Churni. (b) The triangle enclosed by the Railway lines going to Bongaon and Banpur and villages Roynagar and Hijuli.

Chakdah—On the west and north west part.

Haringhata—On the west of Chakdah-Haringhata Road.

2. GANGA FLAT LANDS

These are formed of soils on young alluvial fans, old flood plains or other secondary deposits, having somewhat developed profiles, underlain by unconsolidated material. These profiles show slight compaction and slight accumulation of clay in the subsoils as a result of leaching from the surface horizon. The soils of this "Series" examined are situated in the following Police Stations :

Karimpore—Northern part of the P. S. lying north of the road from Karimpore to the Ferry Ghat on the Mathabhanga at Raghunathpur.

Kaliganj—South western part of the P. S. lying south-west of the road from Kaliganj to Bhaga.

Nakasipara—North eastern and central part of the P. S. The area is roughly from Khajuria to Gotpara, to Bhaga to G. T. S. at Chotasimulia, to Uttar Bahirgachi, to Patkiabari to Nakasipara and Khajuria.

Chapra—Southern part lying south of the line from Basuandulia to Padmamala.

Hanskhali—In the north west and southern part.

Ranaghat—In the northern part and south east part.

3. GANGA LOW LANDS

This is comprised of soils on lower plains, depressions, left river beds, having a good accumulation of clay in the surface soil, underlain by unconsolidated material or more often riverine profile. These are clay pan soils, in which pans are relatively near the surface and relatively impervious to the downward movement of water. Water moves through big cracks in the soil. This is underlain by a horizon, at places of lime, or lime-iron, which do not soften or disintegrate in water. This again is followed by a riverine profiles. Soils of this series occur in the following Police Stations :

Karimpore—Entire southern portion, south of the road taking off from Ferrey Ghat. Narayanpur to Karimpur to Raghunathpur on Mathabhanga.

Tehatta—Entire north and northern part, east of the road from G. T. S. Krishnagar to Tehatta to Taranipur and the east of the loop of Jalangi.

Chapra—North eastern corner bounded by Tehatta-Chapra road and a line approximately from Basandulia to Padmamala situated on Chapra-Bajitpur Road.

Hanskhali—On the south east and north west corners.

Ranaghat—On its east and north-east portion.

Chakdah—On its south eastern fringe.

Haringhata—Its eastern half.

SOIL PHASES

The Association of Ganga Riverine Lands have two phases:

1. Inundated phase.
2. Highland phase.

1. *Inundated phase*—Ganga char lands. This phase of riverine land is found adjacent to the banks of the Ganga, Jalangi, Mathabhanga, Churni and Ichhmati and represents a soil which remains invariably submerged below water during rainy season. The soil is generally of a sandy nature, Typical of the sand bed of the river. The water-table in this region is very high, about 5 to 6 ft. The soils are shallow and are of calcareous nature. No progress of soil-forming process is visible in these areas. Wherever thin layers of silt has been deposited cultivation of early Aus, watermelon and patal is widely practised. Yearly silt deposition keeps up fertility.

2. *Highland phase*—Ganga ridges. The soils are brown in colour, subsoils are usually sand. The region generally suffers from a lack of irrigation facilities, and large areas present thirsty appearance. Loam and loamy sand are the principal textural variations met with. They occur mostly on the highest topography along with the drainage channels. The water table is very low being 15 to 20 ft. in rains and 40 to 50 ft. in summer.

These areas have not been indicated in the map and has been left out for detailed soil survey.

Morphology, mechanical, chemical and general composition of these series have been similar to as have been found for the same soil series occurring in the District of Murshidabad.¹

For the purpose of soil mapping, association of these series were taken as unit. The name of the association was assigned to the predominant soil series occurring in the association. The boundaries of soil associations have been indicated either by the river lines or by the boundary lines of the Police Stations. Where these have not been possible, a straight line has been drawn between observed points to indicate the tentative soil boundaries.

The accompanying schematic soil map illustrates the position occupied by these soil regions.

ACKNOWLEDGMENT

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SOIL ASSOCIATION OF THE NADIA DISTRICT (TENTATIVE) WEST BENGAL.

SCALE

+++ GANGA RIVERINE LANDS
+ GANGA FLAT LANDS
/ GANGA LOW LANDS
o PROFILE SITE



PREPARED BY
THE RAPID RECONNAISSANCE SOIL SURVEY
STAFF
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WEST BENGAL
1955.

HALDAR.

FORMATION OF COMPLEX COMPOUNDS BETWEEN CADMIUM HALIDES AND ALKALI HALIDES PART II

SYSTEM $\text{CdCl}_2 - \text{KCl} - \text{H}_2\text{O}$

By

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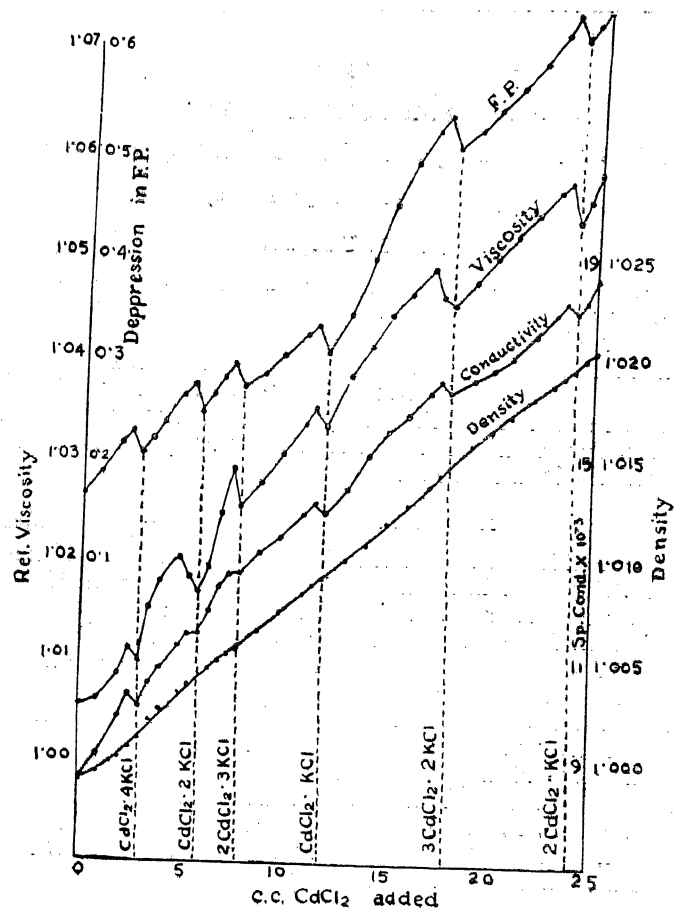
Cadmium Halides are known to form double or complex salts with alkali halides for a long time. In the present communication the formation of complexes between cadmium Chloride and Potassium Chloride is being dealt with. Following the work of K. Von Hauer¹ and H. Croft² who prepared long prismatic crystals of Potassium cadmium trichloride, $\text{KCdCl}_3 \cdot \text{H}_2\text{O}$ various workers^{3,4} tried to investigate the system to find the nature and number of the possible complexes formed either in the solid state or in solution. But no systematic work has yet been done uptill now. So it was thought desirable to take up the work.

EXPERIMENTAL

The substances used were of A. R. quality. Stock solutions of Cadmium Chloride and Potassium Chloride were prepared by dissolving the calculated amounts of the respective salts in conductivity water to form M/4 solutions. The method of monovariation of Nayar and Pande⁵ which consists in keeping the concentration of one of the constituents constant and varying the other systematically was adopted to prepare the subsequent solutions. A 50 cc standard flask was taken and 12 cc of Potassium Chloride was run into it from a burette. The requisite volume of Cadmium Chloride was then added and the volume made up to 50 cc with conductivity water. In this way 35 mixed solutions were prepared in all of which the concentration of KCl was kept constant while the other varied systematically from O. M. to 0.125 M. (0 cc to 25 cc). The solutions were kept in steamed reagent bottles. These solutions were then subjected to careful study by conductivity, viscosity and freezing point methods. The conductivity and viscosity measurements were carried out in an electrically maintained thermostant the temperature of which was kept constant at $30 \pm 1^\circ\text{C}$. The freezing points were determined by using the Beckmann F. P. apparatus. The temperature of the cooling bath was maintained at $-5 \pm 1^\circ\text{C}$ by the addition of ice or salt as the case may be so as to avoid excessive super cooling. 10 cc of the solution was used for each determination, the average of 3 determinations being taken as the correct one.

SUMMARY OF RESULTS

In all the methods the results obtained were plotted against the volume of the variant. All the methods yielded the same type of graphs showing breaks at exactly the same points indicating the formation of six complexes in solution namely, $\text{CdCl}_2 \cdot 4\text{KCl}$, $\text{CdCl}_2 \cdot 2\text{KCl}$, $2\text{CdCl}_2 \cdot 3\text{KCl}$, $\text{CdCl}_2 \cdot \text{KCl}$, $3\text{CdCl}_2 \cdot 2\text{KCl}$ and $2\text{CdCl}_2 \cdot \text{KCl}$. Of these only those with ratios 1:4, 1:2, 1:1.5 and 1:1 have been reported earlier. The other two namely $3\text{CdCl}_2 \cdot 2\text{KCl}$ and $2\text{CdCl}_2 \cdot \text{KCl}$ appear to be new compounds. Further work in the same direction is being done by e. m. f. measurements and absorption spectra studies. Efforts are also being made to isolate the compounds if possible.



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ROLE OF TRACE ELEMENTS IN NITROGEN FIXATION

By

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(Received on 16th June 1956)

INTRODUCTION

The importance of the part of the trace elements in the Science of Agriculture is well recognised now. Quite a good number of plant diseases and other plant conditions are attributed to the shortage or the lack of trace elements in the soil. Some⁽¹⁻³⁾ of them have been found to be somewhat linked with the nitrogen economy of the soil also. This work has been carried out with a view to study the effect of certain trace elements like Molybdenum Vanadium etc. on the fixation of nitrogen caused by the partial oxidation of the energy rich material like Sawdust and plant leaves when added to the soil.

EXPERIMENTAL PROCEEDURE

The soil used in this work was taken from a plot in front of the Sheila Dhar Institute of Soil Science, Allahabad. 200 grams of powdered soil after being passed through a sieve of 80 mesh per inch were taken in 250 c.c. beakers. To this soil 0.5% carbon in the form of well powdered Sawdust was added. To this mixture of the soil and the carbonaceous material, 0.005% and 0.01% of either molybdenum as Potassium molybdate or Vanadium as Vanadium pentoxide or boron as borax or zinc as zinc chloride were added. These beakers were placed under a 500 Watt electric bulb hung over the table at a distance of 2½ feet. A similar set of beakers containing the same amounts of materials were placed besides these beakers covered with a thick black cloth. The moisture of the system was maintained at 20%. The contents of the beakers were stirred on every alternate day with a glass rod in order to facilitate the oxidation of the organic matter. Carbon, nitrogen and the Azotobacter counts of the exposed materials were first determined after three months and then after another three months.

The total carbon present in the system was estimated by the method described by Robinson, McLean and Williams⁽⁴⁾. The total nitrogen was determined by Salicylic Acid reduction method⁽⁵⁾. The Azotobacter counts were determined by Beijerincks medium. All the soil samples were oven dried before analyses.

Soil Analysis			Analysis of Sawdust		
Loss on Ignition	=	7.25%			
HCl Insoluble	=	73.1%			
Sesquioxide	=	9.1%	Ash	=	10.84%
Fe ₂ O ₃	=	3.43%	Silica	=	4.34%
CaO	=	4.31%	Sesquioxide	=	1.589%
MgO	=	1.71%	CaO	=	1.17%

Soil Analysis			Analysis of Sawdust		
K ₂ O	=	1.14%	MgO	=	0.6728%
P ₂ O ₅	=	0.413%	K ₂ O	=	1.278%
Total Carbon	=	1.7453%	P ₂ O ₅	=	0.387%
Total Nitrogen	=	0.2373%	Total Carbon	=	45.23%
Azotobacter Counts	=	2.8 millions per gram	Total Nitrogen	=	0.843%

The following are the tables giving the experimental results of the above soil and sawdust.

Table No. 1 200 grams soil + 0.5% Carbon as Sawdust

Period of exposure in days	Total Carbon %	Carbon Oxidized %	Total Nitrogen %	Increase in Nitrogen %	Efficiency	Azotobacter millions per gram
Exposed						
0	2.2241		0.2439			2.8
90	1.9395	0.2846	0.2672	0.0233	81.8	—
180	1.8527	0.3714	0.2737	0.0298	80.2	5.9
Covered						
0	2.2241		0.2439			2.8
90	2.0507	0.1734	0.2511	0.0072	41.5	—
180	1.9928	0.2313	0.2533	0.0094	40.6	8.1

Table No. 2 200 grams soil + 0.5% C + 0.005% Molybdenum as Potassium Molybdate

Exposed						
0	2.2242		0.2439			2.1
90	1.8617	0.3625	0.2770	0.0331	91.3	—
180	1.7305	0.4937	0.2880	0.0441	89.3	9.1
Covered						
0	2.2242		0.2439			2.8
90	1.9373	0.2869	0.2576	0.0137	47.7	—
180	1.8061	0.4181	0.2634	0.0195	46.6	18.1

Table No. 3 200 grams soil + 0.5% C + 0.01% Molybdenum as Potassium molybdate

Period of exposure in days	Total Carbon %	Carbon Oxidized %	Total Nitrogen %	Increase in Nitrogen %	Efficiency	Azotobacter milli- ons per gram
Exposed						
0	2.2241		0.2438			2.8
90	1.8504	0.3737	0.2793	0.0355	94.9	—
180	1.7216	0.5025	0.2907	0.0469	93.3	9.4
Covered						
0	2.2241		0.2438			2.8
90	1.9306	0.2935	0.2581	0.0143	48.7	—
180	1.8010	0.4231	0.2639	0.0201	47.5	18.8

Table No. 4 200 grams soil + 0.5% C + 0.005% Vanadium as Vanadium pentoxide

Exposed						
0	2.2241		0.2439			2.8
90	1.8792	0.3449	0.2741	0.0302	87.5	—
180	1.7549	0.4692	0.2846	0.0407	86.7	8.7
Covered						
0	2.2241		0.2439			2.8
90	1.9570	0.2671	0.2559	0.0120	44.9	—
180	1.8264	0.3977	0.2612	0.0173	43.5	17.6

Table No. 5 200 grams soil + 0.5% C + 0.01% Vanadium as Vanadium pentoxide

Exposed						
0	2.2242		0.2439			2.8
90	1.8701	0.3541	0.2766	0.0327	92.3	—
180	1.7472	0.4770	0.2874	0.0435	91.1	8.9
Covered						
0	2.2242		0.2439			2.8
90	1.9499	0.2743	0.2569	0.0130	47.3	—
180	1.8209	0.4033	0.2627	0.0188	46.6	18.0

Table No. 6 200 grams soil + 0.5% + 0.005% Boron as Borax

Period of exposure in days	Total Carbon %	Carbon Oxidized %	Total Nitrogen %	Increase in Nitrogen %	Efficiency	Azotobactor milli- ons per gram
Exposed						
0	2.2242		0.2439			2.8
90	1.8991	0.3251	0.2716	0.0277	85.2	—
180	1.7846	0.4396	0.2809	0.0370	84.1	6.9
Covered						
0	2.2242		0.2439			2.8
90	1.9725	0.2517	0.2547	0.0108	42.9	—
180	1.8547	0.3695	0.2594	0.0155	41.9	12.1

Table No. 7 200 grams soil + 0.5% C + 0.01% Boron as Borax

Exposed						
0	2.2242		0.2440			2.8
90	1.8878	0.3364	0.2736	0.0296	87.9	—
180	1.7759	0.4483	0.2829	0.0389	86.7	7.1
Covered						
0	2.2242		0.2440			2.8
90	1.9657	0.2585	0.2553	0.0113	43.7	—
180	1.8505	0.3737	0.2600	0.0160	42.8	12.2

Table No. 8 200 grams soil + 0.5% C + 0.005% Zinc as Zinc Chloride

Exposed						
0	2.2241		0.2440			2.8
90	1.9056	0.3185	0.2705	0.0265	83.2	—
180	1.7906	0.4335	0.2800	0.0360	83.04	6.7
Covered						
0	2.2221		0.2440			2.8
90	1.9813	0.2428	0.2542	0.0102	42.0	—
189	1.8852	0.3389	0.2578	0.0138	40.7	11.8

Table No. 9. 200 grams Soil + 0.5 % C + 0.01 % Zinc as Zinc Chloride

Period of exposure in days	Total carbon %	Carbon oxidized %	Total nitrogen %	Increase in nitrogen %	Efficiency	Azotobacter millions per gram
Exposed						
0	2.2240		0.2441			2.8
90	1.8958	0.3282	0.2724	0.0283	86.2	...
180	1.7809	0.4431	0.2818	0.0377	85.08	6.8
Covered						
0	2.2240		0.2441			2.8
90	1.9722	0.2518	0.2550	0.0109	43.2	...
180	1.8794	0.3446	0.2588	0.0147	42.6	12.0

DISCUSSION

A perusal of the foregoing experimental results indicates that the elements like Mo, V, B & Zn when used in conjunction with organic matter like sawdust enhance the efficiency (the amount of nitrogen fixed in ingms per gram of carbon oxidized) of the process of nitrogen fixation. As has been reported by previous workers the efficiency of nitrogen fixation is always higher in the experiments carried out in light than in the dark.

There is a change in the oxidation of the energy rich substance *i.e.* sawdust on the addition of these minor elements. Higher dose of these elements induces a greater oxidation of the organic matter although the difference in the oxidation caused by the two doses is not large. Molybdenum causes the highest increase in oxidation, second comes vanadium & then boron & zinc. Dhar & Palit ⁽⁶⁾ also obtained increased oxidation of the carbohydrate, by a mixture of iron and copper compounds.

As stated above, the efficiency of nitrogen fixation increases on the addition of these minor elements. There is only a slight increase in the efficiency of nitrogen fixation with the higher concentration of these micronutrients which points out that they are needed in very small amounts. Molybdenum shows the highest increase while vanadium is the second best. Boron is superior to zinc. Thus the order in which these elements increase the efficiency of nitrogen fixation is as follows Mo > V > B > Zn.

Of all these four elements molybdenum appears to be more intimately connected with the nitrogen content of the soil, because as observed, it causes the maximum fixation of nitrogen. It seems to be essential for the symbiotic ⁽⁷⁾ and the non-symbiotic nitrogen fixation processes also. Applications of molybdenum increased the nitrogen content of alfalfa ⁽⁸⁾ in New Jersey from 2.88 to 3.08 % as an average of five cuttings over a period of two years. Mulder ⁽⁹⁾ also observed that white and subterranean clover responded to molybdenum in his pot experiments.

These trace elements i.e. molybdenum, vanadium, boron and zinc increase the Azotobacter population also but their number is invariably greater in dark than in light. Molybdenum has the maximum effect on the growth of their population, the other three come in the following order vanadium > Boron > Zinc.

It may be concluded that the addition of the small amounts of these trace elements in combination with the organic matter like sawdust is an encouraging proposition from the nitrogen point of view.

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INFLUENCE OF CHEMICAL CONSTITUTION ON THE ROTATORY POWER OF OPTICALLY ACTIVE COMPOUNDS

PART I. MANGANESE, IRON, COBALT AND NICKEL SALTS OF *d*-CAMPHOR- β -SULPHONIC ACID

By

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Read at the meeting of the Saugar Branch on 29th September 1953

Several inorganic salts of *d*-camphor- β -sulphonic acid have been prepared and their rotatory power studied in aqueous solution by various workers¹. In the present communication we have described the results of our study on the rotatory dispersion of manganese, iron, cobalt and nickel salts of *d*-camphor- β -sulphonic acid.

EXPERIMENTAL

1. *d*-camphor- β -sulphonic acid. The acid was prepared and purified by the method described by Reychler².

2. *Manganese-d*-camphor- β -sulphonate. *d*-camphor- β -sulphonic acid was dissolved in water and the solution was boiled. To this hot solution was added an excess of freshly prepared manganous hydroxide. Heating was continued for two minutes more and then this hot solution was filtered. The filtrate was concentrated to one fourth of its volume and cooled under tap when crystals of manganese salt separated out. They were filtered at the pump and repeatedly crystallised out of water.

Manganese salt crystallises with six molecules of water of crystallisation as white needles with light pink shade. It is found to give up a major part of its water of crystallisation when heated at 100°C for some time. It is soluble in water, methyl alcohol, ethyl alcohol and pyridine and insoluble in acetone, ether, benzene, toluene, chloroform, carbon tetrachloride, ethyl acetate and glacial acetic acid.

Formula $(C_{10}H_{15}O_4S)_2 \cdot Mn \cdot 6H_2O$ requires, S=10.24%, Mn=8.8%. Found, S=10.25%, Mn=9.03%

3. *Ferrous-d*-camphor- β -sulphonate³. Iron salt was prepared by the same method as described in the case of manganese salt.

It crystallises as pale green needles with six molecules of water of crystallisation which is given off when heated at 140°C for 24 hours. It is soluble in water, ethyl alcohol, methyl alcohol and pyridine and insoluble in acetone, ether, benzene, toluene, chloroform, carbon tetrachloride, ethyl acetate and glacial acetic acid.

Formula $(C_{10}H_{15}O_4S)_2 \cdot Fe \cdot 6H_2O$ requires S=10.22% and mol. wt. = 624.84. Found, S=10.23% and mol. wt. = 627.5.

4. *Cobalt-d*-camphor- β -sulphonate. Cobalt salt was prepared by the interaction of cobalt carbonate and *d*-camphor- β -sulphonic acid by a similar method as used in the case of manganese salt.

Cobalt salt crystallises as pink needles with six molecules of water of crystallisation. It is soluble in water, methyl alcohol, ethyl alcohol and pyridine and insoluble in acetone, ether, benzene, toluene, chloroform, carbon tetrachloride, ethyl acetate and glacial acetic acid.

Formula $(C_{10}H_{15}O_4S)_2 \cdot Co \cdot 6H_2O$ requires $S=10.19\%$. Found, $S=10.14\%$.

5. *Nickel-d-camphor-β-sulphonate*.⁴ This salt was prepared in the same way as the cobalt salt.

It crystallises as light green needles with six molecules of water of crystallisation. It is soluble in water, methyl alcohol, ethyl alcohol and pyridine and insoluble in acetone, ether, benzene, toluene, ethyl acetate, chloroform, carbon tetrachloride and glacial acetic acid.

Formula $(C_{10}H_{15}O_4S)_2 \cdot Ni \cdot 6H_2O$ requires $S=10.18\%$ and $Ni=9.3\%$. Found, $S=10.16\%$ and $Ni=9.6\%$.

The rotatory power determinations were made in a two decimeter polarimeter tube at room temperature (approximately 30°C). The values of λ_0 which were calculated from the dispersion formulae are given in tables I to IV and are expressed as μ or 10^{-4} cm.

Only a limited number of observations could be made in the case of manganese salt in pyridine solution owing to the strong absorptive power of this solution. Rotatory dispersion studies of iron, cobalt and nickel salts in pyridine solutions could not be carried out as these solutions were dark coloured with yellow, pink and green tinge respectively.

DISCUSSION

A. *Nature of the rotatory power.*

The rotatory dispersion of these salts has been determined in the visible region of the spectrum for eleven wavelengths (λ_{6708} Å° U. to λ_{4358} Å° U.) in various solvents and the results will be found recorded in tables I to IV. Analysis of this data was carried out by methods suggested by T. N. Lowery⁵ in his book "Optical Rotatory Power". It was noticed that whether we apply the graphical method or the rigorous algebraic analysis the rotatory dispersion of these salts of *d*-camphor-β-sulphonic acid is always found to be "simple" and follows Drude's one-term equation $[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}$. In this equation K and λ_0 are constants and represent the "absolute" rotation of the substance under examination and the wavelength of the dominant absorption band of its molecule in the ultraviolet region of the spectrum respectively.

The observed values of the optical rotatory power (O) for different wavelengths very closely agree with the corresponding calculated values (C). The tables I to IV show that but for Hg_{4358} which is rather a difficult line to read the differences between the observed and the calculated values of rotatory power are of the nature of casual experimental errors.

B. *Effect of solvent on the rotatory power.*

Manganese salt. The order of rotatory power in different solvents is as follows:—

Methyl Alcohol > Ethyl Alcohol > Pyridine > Water

This sequence is in the reverse order of the dielectric constants of solvents except for pyridine and methyl alcohol.

Iron, Cobalt and Nickel Salts. In these cases the order is : —

Methyl Alcohol > Ethyl Alcohol > Water

This sequence is again in the reverse order of the dielectric constants of the solvents employed except for methyl alcohol.

A reference to the available literature on this topic shows that no rational basis has so far been evolved connecting the nature of the solvent with its effect on the rotatory power of a compound. Various physical constants like the dielectric constant and others of a solvent have been suggested and tried to compare their effect on the change of rotatory power but no definite rule has emerged upto now. Singh⁶ has, however, suggested that instead of forming the dielectric constant as the basis for comparison it will be more rational to use the dielectric constants of their solutions for comparing the results of rotatory dispersion.

C. *Effect of Chemical Constitution on the Rotatory Power.*

The specific rotatory powers, $\left[\alpha \right]_{5461}^{30}$, of Mn, Fe, Co and Ni salts of *d*-

camphor- β -sulphonic acid in different solvents are given in table V. It will be seen that for λ_{5461} in water, ethyl alcohol and methyl alcohol (where a comparison is possible) Mn salt has the highest value for the specific rotatory power whereas the Co salt has the lowest value. The order of decreasing rotatory power is $\text{Mn} > \text{Fe} > \text{Ni} > \text{Co}$. This shows that this sequence of specific rotatory power for these solvents is exactly in the reverse order of the atomic weights of the elements concerned. The same order holds if specific rotations corresponding to other wavelengths for which observations have been recorded in tables I to IV are compared. A somewhat similar conclusion has been arrived at by Perti and Murty⁷ who have studied the rotatory dispersion of Mg, Ca, Sr and Ba salts of Reychler's acid.

It is, however, interesting to note that Graham⁸ has arrived at a different conclusion, on the basis of his work on Mg, Cd and Cu salts of *d*-camphor- β -sulphonic acid, when he stated that the atomic weight of the metal in combination cannot be an important factor in this question of change of rotatory power.

It may also be noted that if the comparison of the specific rotatory power of these compounds is made on the basis of the position of these elements in the electromotive series of metals a different order is followed. Whereas the order of the decreasing rotatory power is $\text{Mn} > \text{Fe} > \text{Ni} > \text{Co}$, the order of the decreasing electropositive nature of the elements is $\text{Mn} (-1.04) > \text{Fe} (-0.44) > \text{Co} (-0.29) > \text{Ni} (-0.22)$. So it follows that the order of decreasing specific rotatory power runs parallel to the decreasing order of the electropositive nature of the elements except for Ni.

A similar comparison of the specific rotatory power with the atomic numbers of the elements involved can also be made. Here the order of decreasing rotatory power of these compounds is in the reverse order of the atomic numbers of the elements concerned except for Ni. The increasing order of their atomic numbers being $\text{Mn} (25) < \text{Fe} (26) < \text{Co} (27) < \text{Ni} (28)$.

SUMMARY

1. The rotatory dispersion of Mn, Fe, Co and Ni salts of *d*-camphor- β -sulphonic acid has been studied and is found to be simple.
2. The influence of substituting different elements in the inorganic salts of *d*-camphor- β -sulphonic acid has been investigated.
3. The effect of solvent on the rotatory power of a compound has also been studied.

ACKNOWLEDGEMENT

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TABLE I
Manganese-d-camphor-β-sulphonate

Solvent	Water	Pyridine	Ethyl Alcohol	Methyl Alcohol								
Concentration in gm./100 C. G.	1·0000	1·0000	1·0000	1·0000								
Calculated	$[\alpha] = \frac{5·193}{\lambda^2 - 0·1390} - \frac{5·709}{\lambda^2 - 0·1290} + \frac{6·153}{\lambda^2 - 0·1310}$ $\lambda_0 \quad 0·3728 \quad 0·3592 \quad 0·3688 \quad 0·3619$											
Line	Obs. [α] (O)	Cal. [α] (C)	O - C	Obs. [α] (O)	Cal. [α] (C)	O - C						
Li6708	+17·00	+16·69	+0·31	+17·50	+17·78	+0·28	+18·50	+17·82	+0·68	+19·50	+19·29	+0·21
Cd6438	19·00	18·85	+0·15	20·00	19·99	+0·01	20·50	20·09	+0·41	22·00	21·70	+0·30
Li6104	21·50	22·24	-0·74	23·00	23·44	-0·44	23·50	23·67	-0·17	25·00	25·48	-0·48
Na5893	25·00	24·94	+0·06	26·00	26·16	-0·16	26·50	26·50	0·00	28·50	28·45	+0·05
Hg5780	26·00	26·62	-0·62	28·50	27·83	+0·67	29·00	28·25	+0·75	30·50	30·30	+0·20
Hg5461	33·00	32·61	+0·39	34·00	33·74	+0·26	34·50	34·50	0·00	36·00	36·81	-0·81
Cd5085	43·00	43·38	-0·38	44·00	44·00	0·00	45·00	45·61	-0·61	47·56	48·18	-0·68
Cd4799	57·00	56·82	+0·18	—	—	—	59·50	59·28	+0·22	61·50	61·90	-0·40
Cd4678	65·00	65·00	0·00	—	—	—	67·50	67·50	0·00	70·00	70·00	0·00
Li4602	71·00	71·34	-0·34	—	—	—	73·50	73·82	-0·32	76·00	76·15	-0·15
Hg4358	103·00	101·80	+1·20	—	—	—	106·00	103·60	+2·40	105·50	104·20	+1·30

TABLE II

Ferrous-d-camphor-β-sulphonate

Solvent	Water	Ethyl Alcohol	Methyl Alcohol						
Concentration in gm./100 C.G.	1·0000	1·0000	1·0000						
[α]									
Calculated	$\frac{4·655}{\lambda^2·0·1450}$	$\frac{5·513}{\lambda^2·0·1360}$	$\frac{5·957}{\lambda^2·0·1280}$						
λ_0	0·3808	0·3688	0·3578						
Line	Obs. [α] (O)	Cal. [α] (C)	O-C	Obs. [α] (O)	Cal. [α] (C)	O-C			
Li ₆₇₀₈	+15·00	+15·26	- 0·26	+17·00	+17·56	- 0·56	+18·50	+18·49	+0·01
Cd ₆₄₃₈	17·00	17·27	- 0·27	20·00	19·80	+0·20	21·00	20·79	+0·21
Li ₆₁₀₄	20·00	20·46	- 0·46	23·00	23·31	- 0·31	24·00	24·36	- 0·36
Na ₅₈₉₃	23·00	23·02	- 0·02	26·00	26·10	- 0·10	27·00	27·17	- 0·17
Hg ₅₇₈₀	25·00	24·61	+0·39	27·50	27·83	- 0·33	28·50	28·90	- 0·40
Hg ₄₅₆₁	30·00	30·38	- 0·38	34·00	33·99	+0·01	35·00	35·00	0·00
Cd ₅₀₈₅	40·50	40·95	- 0·45	44·50	44·93	- 0·43	45·00	45·59	- 0·59
Cd ₄₇₉₉	53·00	54·50	- 1·50	58·00	58·39	- 0·39	-	-	-
Cd ₄₆₇₈	63·00	62·99	+0·01	66·50	66·49	+0·01	-	-	-
Li ₄₆₀₂	70·00	69·68	+0·32	72·50	72·73	- 0·23	-	-	-
Hg ₄₃₅₈	103·00	103·50	- 0·50	104·00	102·10	+1·90	-	-	-

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TABLE III

Nickel-d-camphor-β-sulphonate

Solvent	Water	Ethyl Alcohol	Methyl Alcohol
Concentration in gm./100 C. C.	1·0000	1·00000	1·0000
$[\alpha]$	3·301 $\lambda^2-0·1490$	4·076 $\lambda^2-3·1420$	4·437 $\lambda^2-0·1390$
Calculated λ_0	0·3860	0·3768	0·3728

Line	Obs. $[\alpha]$ O	Cal. $[\alpha]$ (C)	O—C	Obs. (α) (O)	Cal. $[\alpha]$ (C)	O—C	Obs. $[\alpha]$ (O)	Cal. $[\alpha]$ (C)	O—C
Li ₆₇₀₈	+11·50	+10·96	+0·54	+13·50	+13·23	+0·27	+15·00	+14·27	+0·73
Cd ₆₄₃₈	12·50	12·44	+0·06	15·00	14·96	+0·04	16·50	16·11	+0·39
Li ₆₁₀₄	15·00	14·77	+0·23	17·50	17·68	-0·18	20·00	19·00	+1·00
Na ₅₈₉₃	17·00	16·65	+0·35	20·00	19·86	+0·14	21·50	21·31	+0·19
Hg ₅₇₈₀	18·00	17·83	+0·17	21·50	21·21	+0·29	22·50	22·75	-0·25
Hg ₅₄₆₁	22·00	22·12	-0·12	26·00	26·09	-0·09	28·00	27·36	+0·64
Cd ₅₀₈₅	30·50	30·09	+0·41	35·00	34·92	+0·08	37·00	37·07	-0·07
Cd ₄₇₉₉	40·50	40·55	-0·05	46·50	46·10	+0·40	48·50	48·55	-0·05
Cd ₄₆₇₈	48·50	47·22	+1·28	53·00	53·01	-0·01	54·50	55·54	-1·04
Li ₀₄₆₂	53·00	52·55	+0·45	58·50	58·38	+0·12	61·00	60·95	+0·05
Hg ₄₃₅₈	80·50	80·50	0·00	86·00	84·92	+1·08	87·00	87·00	0·00

TABLE IV

Cobalt-d-camphor-β-sulphonate

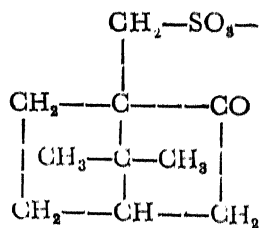
Solvent	Water	Ethyl Alcohol	Methyl Alcohol						
Concentration in gm./100 C. G	1.000	1.0000	1.0000						
Calculated	$[\alpha] = \frac{3.200}{\lambda^2 - 0.1500}$ $\lambda_0 = 0.3873$	$= \frac{3.686}{\lambda^2 - 0.1480}$ 0.3847	$\frac{4.152}{\lambda^2 - 0.1420}$ 0.3768						
Line	Obs. $[\alpha]$ (O)	Cal. $[\alpha]$ (G)	O - G	Obs. $[\alpha]$ (O)	Cal. $[\alpha]$ (G)	O - G	Obs. $[\alpha]$ (O)	Cal. $[\alpha]$ (G)	O - G
Li ₆₇₀₈	+10.50	+10.67	-0.17	+12.50	+12.21	+0.29	+13.50	+13.48	+0.02
Cd ₆₄₃₈	11.50	12.10	-0.60	14.50	13.83	+0.67	15.50	15.24	+0.26
Li ₆₁₀₄	15.00	14.38	+0.62	17.00	16.43	+0.57	17.50	18.01	-0.51
Na ₅₈₉₃	16.50	16.23	+0.27	18.50	18.50	0.00	20.00	20.23	-0.23
Hg ₅₇₈₀	17.00	17.39	-0.39	20.00	19.81	+0.19	21.50	21.61	-0.11
Hg ₅₄₆₁	21.50	21.59	-0.09	24.50	24.54	-0.04	26.50	26.58	-0.08
Cd ₅₀₈₅	30.00	29.44	+0.56	33.00	33.32	-0.32	36.00	35.57	+0.43
Cd ₄₇₉₉	40.00	39.80	+0.20	45.00	44.74	+0.26	47.50	46.96	+0.54
Cd ₄₆₇₈	46.50	46.45	+0.05	52.00	52.00	0.00	54.00	53.99	+0.01
Li ₆₄₀₂	52.50	51.78	+0.72	58.00	57.79	+0.21	60.00	59.47	+0.53
Hg ₄₃₅₈	80.00	80.00	0.00	85.00	87.78	-2.78	86.50	86.50	0.00

TABLE V

No.	Compound	$[\epsilon]_{5461}^{30^\circ}$			
		Water 80*	Pyridine 12.4*	Ethyl Alcohol 25.8*	Methyl Alcohol 31.2*
1.	$R_2^\dagger \text{Mn} \cdot 6 \text{H}_2\text{O}$	33.00 (5.193) ††	34.00 (5.709)	34.50 (5.597)	36.00 (6.153)
2.	$R_2 \text{Fe} \cdot 6 \text{H}_2\text{O}$	30.00 (4.655)	— —	34.00 (5.513)	35.00 (5.957)
3.	$R_2 \text{Ni} \cdot 6 \text{H}_2\text{O}$	22.00 (3.301)	— —	26.00 (4.076)	28.00 (4.437)
4.	$R_2 \text{Co} \cdot 6 \text{H}_2\text{O}$	21.50 (3.200)	— —	24.50 (3.686)	26.50 (4.152)

*These values refer to the dielectric constants.

$^\dagger R$ stands for



†† The values in brackets stand for the rotation constants.

INFLUENCE OF CHEMICAL CONSTITUTION ON THE ROTATORY POWER OF OPTICALLY ACTIVE COMPOUNDS

PART II. PHENYL -, *o*-NITROPHENYL -, *p*-NITROPHENYL- and 2; 4-DINITROPHENYL HYDRAZONES OF *d*-CAMPHOR- β -SULPHONIC ACID

By

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Various organic and inorganic¹ salts of *d*-camphor- β -sulphonic acid have been prepared by several investigators and their rotatory powers studied from different angles. Generally it is observed that the derivatives of the *d*-acid are dextrorotatory in nature and those obtained from its laevo isomer are laevorotatory.

Fernandes and Castillo², however, while preparing 2:4-dinitrophenylhydrazone of *d*-camphor- β -sulphonic acid came across a significant phenomenon. The acid gave two varieties of 2:4-dinitrophenylhydrazones under different experimental conditions: the yellow form, m. p. 215°C and $[\alpha]_D - 130^\circ$ in dilute ethyl alcohol; and the red form, m. p. 193-195°C and optically inactive. A somewhat similar observation was made by Schreiber and Shriner³ who noticed that *d*-camphor- β -sulphonic acid phenylhydrazone which was previously prepared by Reychler⁴, m. p.

235-242°C, has $[\alpha]_D^{25} - 185.3^\circ$ in 1:1 methyl alcohol and chloroform mixture.

The formation of laevorotatory phenylhydrazones from *d*-camphor- β -sulphonic acid being an exquisite phenomenon a study of this type of compounds was undertaken. Phenyl-, *o*-nitrophenyl-, *p*-nitrophenyl- and 2:4-dinitrophenylhydrazones were prepared and their rotatory dispersion studied.

EXPERIMENTAL

1. *d*-Camphor- β -sulphonic acid phenylhydrazone^{3,4}

Molar proportions of phenylhydrazine and *d*-camphor- β -sulphonic acid were dissolved in ethyl alcohol separately. The two solutions were then mixed. The mixture was then concentrated by evaporation when white leaflets with greenish tinge of phenylhydrazone separated out on scratching. They were repeatedly recrystallised out of glacial acetic acid and ethyl alcohol mixture and finally dried in vacuum.

The *d*-camphor- β -sulphonic acid phenylhydrazone is soluble in pyridine (yellow solution), sparingly so in methyl alcohol, ethyl alcohol, ethyl acetate, glacial acetic acid and acetone and practically insoluble in water, chloroform, carbon tetrachloride, ether, benzene etc.

Found, m. p. 238-242°C, S=9.81%, $C_{16}H_{22}N_2O_3$ requires S=9.94%.

2. *d-Camphor-β-sulphonic acid o-nitrophenylhydrazone.*

Molar proportion of *o*-nitrophenylhydrazine was added to a warm alcoholic solution of *d*-camphor-β-sulphonic acid containing molar quantity of the acid. The solution was heated till the *o*-nitrophenylhydrazine completely dissolved and evaporated till most of the alcohol was removed. Sulphuric ether was then added when the hydrazone precipitated out. It was repeatedly recrystallised from a mixture of glacial acetic acid and sulphuric ether as yellow powder.

It is soluble in pyridine (red solution), methyl alcohol (deep orange solution), ethyl acetate (light orange solution) and glacial acetic acid (red solution); sparingly so in acetone (light orange solution) and practically insoluble in ether, chloroform, carbon tetrachloride, benzene etc.

Found, m. p. 225°C, S=8.7%, $C_{18}H_{21}N_3O_5$ requires S=8.48%.

3. *d-Camphor-β-sulphonic acid p-nitrophenylhydrazone*

Molar proportion of *p*-nitrophenylhydrazine was added to a warm alcoholic solution of *d*-camphor-β-sulphonic acid containing its molar quantity. The solution was heated till it was clear and allowed to cool. Ether was then added whereby *p*-nitrophenylhydrazone was precipitated. It was filtered at the pump and was recrystallised out of a mixture of glacial acetic acid and ethyl alcohol as light yellow needles.

It is freely soluble in pyridine giving deep yellow solution and less so in methyl alcohol and ethyl alcohol, sparingly soluble in acetone, ethyl acetate and glacial acetic acid and practically insoluble in water, benzene, ether, chloroform, and carbon tetrachloride.

Found, m. p. 255°d, S=8.4%, $C_{18}H_{21}N_3O_5$ requires S=8.1%.

4. *d-Camphor-β-sulphonic acid 2:4-dinitrophenylhydrazone^a.*

Molar quantity of 2:4-dinitrophenylhydrazine was added to an alcoholic solution of *d*-camphor-β-sulphonic acid containing its molar proportion. The solution was allowed to cool and ether was added when 2:4-dinitrophenylhydrazone precipitated out, it was filtered at the pump and recrystallised out of a mixture of methyl alcohol and nitrobenzene as yellow crystalline needles.

It is freely soluble in pyridine, less so in methyl alcohol, acetone and glacial acetic acid, sparingly soluble in ethyl alcohol and ethyl acetate and practically insoluble in chloroform, carbon tetrachloride, ether, benzene and toluene.

Found, m. p. 215°C, S=7.68%, $C_{18}H_{20}N_4O_7$ requires S=7.75%.

The rotatory power determinations were made in a 2.2 decimeter polarimeter tube at room temperature (30°C). The values of λ_0 calculated from the dispersion formulae, are given in tables I to IV and are expressed as μ or 10^{-4} Cm.

Only a limited number of observations could be made in the cases under investigation owing to the strong absorptive power of their solutions. Rotatory dispersion study of *o*-nitrophenylhydrazone in pyridine could not be carried out because of the dark red colour of the solution.

DISCUSSION

1. *Nature of the rotatory dispersion*

The rotatory dispersion of these hydrazones has been determined in the visible region of the spectrum for several wavelengths in different solvents and the results are recorded in tables I to IV. The dispersion is found to be 'simple' as it follows Drude's one-term equation, $[\alpha] = \frac{K_0}{\lambda^2 - \lambda_0^2}$. In this equation K_0 and λ_0 are constants and represent the absolute rotation of the substance under examination and the wavelength of the dominant absorption band of its molecule in the ultra-violet region of the spectrum respectively.

The observed values of the optical rotatory power (O) for different wavelengths closely agree with the corresponding calculated values (C). These differences are within the experimental error of measurement. These values along with the differences ($O-C$) are recorded in tables I to IV.

2. *The effect of substituent groups on rotatory power*

Rule⁵ has shown that the arrangement of groups according to their polarities follows a general order with minor differences, and that the order is:

OH, Cl, Br, I, NH₂, C₂H₅, CH₃, H, COOH, CHO, COCH₃, CN, NO₂⁺
Since the substitution of polar groups has been shown to modify the rotatory power of an optically active compound, it is observed that in general the replacement of a hydrogen atom by a positive substituent group displaces the rotation in the reverse sense to that due to a negative substituent. Further more, a positive group should cause an increase in rotation and a negative group should depress it.

Table V gives the values of $[\alpha]_{5893}^{30}$ in various solvents. The values of K_0 ,

the rotation constant, are also given. On comparing the values of $[\alpha]_{5893}^{30}$ for the four hydrazones in question in methyl alcohol and pyridine, where a comparison is possible, it is found that in methyl alcohol the substitution of the hydrogen atom by the positive nitro group depresses the rotatory power—the 2:4-dinitro compound having the lowest rotation. The order of decreasing rotation being $Un > p > o > di$. The same order is followed if a comparison of the values of K_0 , the rotation constant, is made.

In pyridine, however, it will be observed that the introduction of the nitro group enhances the rotation of the parent compound. The decreasing order of $[\alpha]_{5893}^{30}$ in pyridine being $p > di > un$. The same sequence is maintained if a comparison of the values of the rotation constants, K_0 , is made. This is in conformity with Rule's generalisation.

3. *The effect of solvent*

The order of specific rotatory power, $[\alpha]_{5893}^{30}$, for the various hydrazones in different solvents is as follows:—

A. *d*-camphor- β -sulphonic acid phenylhydrazone

Methyl alcohol > pyridine

In this case the decreasing order of specific rotatory power runs parallel to the decreasing order of the dielectric constants of the solvents employed.

B. *d*-camphor- β -sulphonic acid *o*-nitrophenylhydrazone

Ethyl alcohol > methyl alcohol > acetone

Here also the decreasing order of rotatory power runs parallel to the decreasing values of the dielectric constants of the solvents except for ethyl alcohol.

C. *d*-camphor- β -sulphonic acid *p*-nitrophenylhydrazone

Pyridine > methyl alcohol > ethyl alcohol

The sequence of rotatory power in this case is also parallel to the order of the dielectric constants of the solvents except for pyridine.

D. *d*-camphor- β -sulphonic acid 2:4-dinitrophenylhydrazone

Methyl alcohol > pyridine > acetone

The order of decreasing rotatory power in this case again runs parallel to the sequence of decreasing dielectric constants of the solvents concerned except for pyridine.

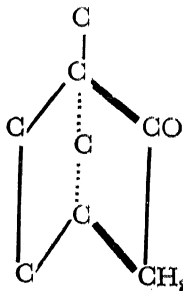
Solvent has been found to profoundly influence the rotatory power of a compound⁶. Different workers have used different physical constants to correlate the influence of the solvent and its effect on the rotatory power of the compound but even upto now precise information concerning the change in optical power caused by the solvent is lacking.

4. *The relation between chemical constitution and optical rotatory power*

Table A gives the values of $[\alpha]_{5893}^{30}$ in methyl alcohol for the four hydrazones under investigation.

A glance at this table shows that in all the four cases the hydrazones possess high laevorotation.

It may be noted that the camphor skeleton which has a bicyclic structure implies a *cis* disposition of the $-\text{CO}-\text{CH}_2$ bridge as shown below :—



The *trans* arrangement, however, is not possible as it involves considerable strain which is not consistent with the stability of the compound and it may be conveniently inferred that the same configuration holds in the case of *d*-camphor- β -sulphonic acid. So during the course of the reaction between the ketonic group of the acid and the hydrazine no profound change in the structure can be expected which may be attributed to the reversal of the sign of rotation in the hydrazone formation.

TABLE A

No.	Compound	$[\alpha]_{5893}^{35}$ in methyl alcohol
1.	$\overset{*}{R} = \text{N.NH} \langle \text{Cyclohexyl} \rangle$	- 185.5°
2.	$R = \text{N.NH} \langle \text{Cyclohexyl-NO}_2 \rangle$	- 150.0
3.	$R = \text{N.NH} \langle \text{Cyclohexyl-NO}_2 \rangle$	- 163.6
4.	$R = \text{N.NH} \langle \text{Cyclohexyl-NO}_2 \rangle$	- 122.7

A possible explanation of this type of change has been suggested by Schreiber and Shriner³. According to these authors all camphor compound having the ketimine structure $>\text{C}=\text{N}-$ are laevorotatory in nature. The only exception to this rule is the anil of camphor^{8,9} which has a dextrorotation of +11.5°. Since all the hydrazones under examination also possess the anil or ketimine structure, their laevorotation further supports the generalisation of Schreiber and Shriner.

ACKNOWLEDGEMENT

The authors are grateful to the University of Saugar for providing research facilities and to the Ministry of Education, Govt. of India for the grant of a senior research scholarship to one of us (S.P.B.)

*R stands for $\text{C}_8\text{H}_{13}\text{SO}_3\text{H} \begin{array}{l} \text{C=O} \\ | \\ \text{CH}_2 \end{array}$

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TABLE I

Phenylhydrazone of d-camphor-β-sulphonic acid.

Solvent	Methyl Alcohol			Pyridine		
Concentration in gr./100 C.C.	0.2500			0.2500		
Calculated	$[\alpha]$	$\frac{61.49}{\lambda^2 - 0.0165}$	$\frac{23.21}{\lambda^2 - 0.0852}$			
	λ_0	0.1277	0.2319			
Line	Obs (O)	Cal (C)	O-C	Obs (O)	Cal (C)	O-C
Li ₆₇₀₈	- 141.8°	- 141.8°	0.00°	- 63.66°	- 63.64°	- 0.04
Cd ₆₄₃₈	154.5	154.4	+0.10	70.90	70.50	+0.40
Li ₆₁₀₄	172.7	172.7	0.00	80.00	80.79	- 0.79
Na ₅₈₉₃	185.5	185.8	- 0.30	89.00	88.62	+ 0.38
Hg ₅₇₈₀	192.7	193.5	- 0.80	92.70	93.26	- 0.56
Hg ₅₄₆₁	218.1	218.1	0.00	109.0	109.0	0.00
Cd ₅₀₈₅	252.7	253.7	- 1.00	134.5	133.9	+0.60
Cd ₄₇₉₉	287.2	287.2	0.00	160.0	159.9	+0.10
Cd ₄₆₄₈	303.6	303.5	+0.10	174.5	173.6	+0.90
Li ₄₆₀₂	314.5	314.6	- 0.10	183.6	183.3	+0.30
Hg ₄₃₄₈	354.2	354.2	+0.30	220.0	221.6	- 1.60

TABLE II

d-Camphor- β -sulphonic acid *o*-nitrophenylhydrazone

Solvent	Ethyl Alcohol		Methyl Alcohol		Acetone	
Concentration in gm/100 C.C.	0.1000		0.1000		0.1000	
Calculated	$\frac{43.36}{\lambda^2 - 0.083}$		$\frac{31.34}{\lambda^2 - 0.137}$		$\frac{19.50}{\lambda^2 - 0.0598}$	
λ_0	0.2881		0.3701		0.2445	
Line	Obs (O)	Cal. (C)	O-C	Obs. (O)	Cal. (C)	O-C
Li ₆₇₀₈	-118.1°	-118.1	0.00	-100.0	-100.0	-0.02
Cd ₆₄₃₈	131.8	130.8	+1.00	113.6	112.9	-0.48
Li ₆₁₀₄	150.0	149.7	+0.30	131.8	133.0	+1.24
Na ₅₈₉₃	163.7	164.2	-0.50	150.0	149.1	+0.25
Hg ₅₇₈₀	172.7	172.7	0.00	159.0	159.0	+1.61
Hg ₅₄₆₁	—	—	—	—	—	-0.01
Cd ₅₀₈₅	—	—	—	—	—	—
Cd ₄₇₄₉	—	—	—	—	—	—
Cd ₄₆₄₈	—	—	—	—	—	—
Li ₄₆₀₂	—	—	—	—	—	—
Hg ₄₃₅₈	—	—	—	—	—	—

TABLE III

d-Camphor- β -sulphonic acid *p*-nitrophenylhydrazone

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TABLE IV
d-Comphor- β -sulphonic acid 2,4-dinitrophenylhydrazone

a-Complan-p-sulphonic acid and *a-Complan-p-sulphonic acid* I

Solvent	Methyl Alcohol		Pyridine		Acetone			
Concentration in gm./100 C. G.	0.1000		0.2500		0.2500			
Calculated	$[\alpha]$ 31.14 λ^2 0.0893 λ_0 0.2988		30.88 λ^2 0.0253 0.1591		23.21 λ^2 0.0852 0.2919			
Line	Obs. (O)	Cal. (G)	O-C	Obs. (G)	O-C	Obs. (O)	Cal. (C)	O-C
Li 6708	-86.3°	-86.34°	-0.04	-72.70°	-0.01°	-63.60°	-63.63°	-0.03°
Cd 6438	95.45	95.74	-0.29	80.00	+0.44	71.80	70.50	+1.30
Li 6104	109.0	110.0	-1.00	89.00	+0.06	80.00	80.79	-0.79
Na 5893	122.7	121.1	+1.60	96.36	+0.42	89.30	88.61	+0.39
Hg 5780	127.3	127.2	+0.10	100.0	0.00	92.70	93.26	-0.56
Hg 5461	150.0	149.0	+1.00	—	—	109.0	109.0	0.00
Cd 585	182.8	183.8	-1.00	—	—	134.5	133.9	+0.60
Cd 4799	—	—	—	—	—	—	—	—
Cd 4648	—	—	—	—	—	—	—	—
Li 4602	—	—	—	—	—	—	—	—
Hg 4358	—	—	—	—	—	—	—	—

TABLE V

Compound	$[\alpha]_{5893}^{30}$			
	Methyl Alcohol (31.2)*	Ethyl Alcohol (25.8)	Acetone (21.5)	Pyridine (12.4)
1. $R^{\dagger} = N.NH<\text{C}_6\text{H}_5>$	185.5 [61.49] $_{\ddagger}$	—	—	89.00 [23.21]
2. $R = N.NH<\text{C}_6\text{H}_4\text{NO}_2>$	150.0 [31.34]	163.7 [43.36]	68.10 [19.50]	—
3. $R = N.NH<\text{C}_6\text{H}_4\text{NO}_2>$	163.6 [43.79]	134.5 [27.36]	—	172.7 [44.14]
4. $R = N.NH<\text{C}_6\text{H}_3\text{NO}_2>$	122.7 [31.14]	—	89.00 [23.21]	96.36 [30.88]

*The figures in brackets refer to the dielectric constants.

$\dagger R$ stands for $C_8H_{19}SO_3H<\text{C}(=\text{O})\text{CH}_2>$

\ddagger The figures in square brackets refer to the rotation constant, K_0 .

ON SELF RECIPROCAL FUNCTIONS

By

V. V. L. NARASIMHA RAO

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Following the notation of Hardy and Titchmarsh, I will call a function $f(x)$ as R_μ if

$$f(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} 2^s \cdot \Gamma\left(\frac{1}{4} + \frac{\mu}{2} + \frac{s}{2}\right) \cdot \psi(s) \cdot x^{-s} ds \quad \dots (1)$$

Where

$$0 < c < 1$$

and

$$\psi(s) = \psi(1-s)$$

Under these conditions, $f(x)$ is said to be self-reciprocal for Hankel transforms of order μ .

2. I will start with the integral

$$\int_0^\infty J_\mu(bt) \frac{\pi \left[J_\nu \left\{ a \sqrt{t^2 + z^2} \right\} \right]}{(t^2 + z^2)^{\frac{n\nu}{2}}} t^{(\mu-1)} dt = \frac{2^{(\mu-1)} \Gamma(\mu)}{b^\mu} \frac{\pi J_\nu(az)}{z^\nu} \quad (2)$$

Where the product is extended to n terms; the conditions under—which the integral is valid are

$$b = \Sigma a$$

$$\text{and } R(n\nu + \frac{1}{2}n + \frac{1}{2}) > R(\mu) > 0.$$

$$\text{Hence } \int_0^\infty 2 b^\mu \cdot J_\mu(bt) \frac{\pi \left[J_\nu \left\{ a \sqrt{t^2 + z^2} \right\} \right]}{(t^2 + z^2)^{\frac{n\nu}{2}}} t^{(\mu-1)} dt = 2^\mu \cdot \Gamma(\mu) \frac{\pi J_\nu(az)}{a} \frac{1}{z^\nu}$$

Therefore applying Mellin's inversion formula, we obtain,

$$2 b^\mu \cdot J_\mu(bt) \frac{\pi \left[J_\nu \left\{ a \sqrt{t^2 + z^2} \right\} \right]}{(t^2 + z^2)^{\frac{n\nu}{2}}} = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} 2^\mu \cdot \Gamma(\mu) \frac{\pi J_\nu(az)}{a} \frac{t^{-\mu}}{z^\nu} d\mu.$$

Where

$$0 < C < 1.$$

...(3)

Putting $\mu = \frac{\lambda}{2}$; $t = y^2$, we obtain

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$$4 b^{\lambda/2} J_{\lambda/2} (b y^2) \frac{\pi}{a} \left[J_{\nu} a \left\{ \sqrt{y^4 + z^2} \right\} \right] \frac{nv}{(y^4 + z^2)^{\frac{2}{2}}} \\ = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} 2^{\lambda/2} \Gamma\left(\frac{\lambda}{2}\right) \frac{\pi}{a} J_{\nu}(az) y^{-\lambda} d\lambda \quad \dots(4)$$

So that

$$\psi(\lambda) = \frac{\pi J_{\nu}(az)}{a z^{\nu}} = \psi(1-\lambda)$$

$$\& \Gamma\left(\frac{1}{4} + \frac{\mu}{2} + \frac{s}{2}\right) = r\left(\frac{\lambda}{2}\right) \text{ giving } \mu = -\frac{1}{2}$$

Hence we find the function

$$4 b^{\lambda/2} J_{\lambda/2} (b y^2) \frac{\pi}{a} \left[J_{\nu} a \left\{ \sqrt{y^4 + z^2} \right\} \right] \frac{nv}{(y^4 + z^2)^{\frac{2}{2}}} \quad \dots(5)$$

represents different self-reciprocal functions, for different values of λ and ν ; and containing the two variables t and y ; Further for each value of λ and ν , different values of a and b can be chosen so that, the above function represents an infinite number of self-reciprocal functions, for different values of λ and ν each function changing with different values of a and b , under the above conditions. And all these functions are $R - \frac{1}{2}$ i.e. R_c .

3. But the conditions required for the above product are not the same for different values of n .

For example let us start with the integral

$$\int_0^{\infty} J_{\mu}(bt) \cdot J_{\nu} \left\{ a \sqrt{t^2 + z^2} \right\} \cdot J_{\lambda} \left\{ a \sqrt{t^2 + z^2} \right\} t^{(\mu-1)} dt \\ \frac{(t^2 + z^2)^{\frac{\lambda+\nu}{2}}}{b^{\mu}} \cdot \Gamma(\mu) \cdot J_{\nu}(az) \cdot J_{\lambda}(az) \quad \dots(6)$$

where

$$b > 2a; \text{ and } R\left(\nu + \lambda + \frac{5}{2}\right) > R\left(\frac{\mu}{2}\right) > 0$$

$$\text{So that } \int_0^\infty 2b^\mu J_\mu(bt) \cdot J_\nu\left(\frac{a\sqrt{t^2+z^2}}{\frac{\lambda+\nu}{2}}\right) \cdot J_\lambda\left(\frac{a\sqrt{t^2+z^2}}{\frac{\lambda+\nu}{2}}\right) t^{(\mu-1)} dt$$

$$= 2^\mu \cdot \Gamma(\mu) \cdot J_\nu(az) J_\lambda(az) \frac{1}{z^{\lambda+\nu}}$$

Hence applying Mellin's inversion formula and putting

$$\mu = \frac{a}{2}; t = y^2, \text{ we obtain,}$$

$$4b^{a/2} \cdot J_{a/2}(by^2) \cdot J_\nu\left(\frac{a\sqrt{y^4+z^2}}{\frac{\lambda+\nu}{2}}\right) \cdot J_\lambda\left(\frac{a\sqrt{y^4+z^2}}{\frac{\lambda+\nu}{2}}\right)$$

$$= \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} 2^{a/2} \Gamma(a/2) \cdot J_\nu(az) J_\lambda(az) \cdot y^{-a} da.$$

$$\text{Where } 0 < c < 1$$

$$\text{So that } \psi(a) = J_\nu(az) J_\lambda(az) = \psi(1-a)$$

$$\text{and } \Gamma\left(\frac{1}{4} + \frac{\mu}{2} + \frac{s}{2}\right) = \Gamma\left(\frac{a}{2}\right) \text{ given } \mu = -\frac{1}{2}.$$

Hence again we find that

$$4b^{a/2} \cdot J_{a/2}(by^2) \cdot J_\nu\left\{\frac{a\sqrt{y^4+z^2}}{\frac{\lambda+\nu}{2}}\right\} \cdot J_\lambda\left\{\frac{a\sqrt{y^4+z^2}}{\frac{\lambda+\nu}{2}}\right\}$$

is self-reciprocal for Hankel transforms of order $-\frac{1}{2}$. As before, giving different values to a , ν , and λ , we find that the above function represents a triply infinite number of S. R. functions all belonging to $R - \frac{1}{2}$. And for each of the above functions, another infinite number can be formed giving different values to a and b , Provided

$$b > 2a \text{ \& } R\left(\nu + \lambda + \frac{5}{2}\right) > R\left(\frac{a}{2}\right).$$

Further, the above function represents a self-reciprocal function in two variables y and z .

4. Again if we start with the formula,

$$\int_0^\infty J_\mu(bt) \cdot J_\nu \left(\frac{a \sqrt{t^2 + z^2}}{(t^2 + z^2)^{\frac{\nu}{2}}} \right) t^{\frac{(\mu-1)}{b^\mu}} = 2^{\frac{(\mu-1)}{z^\nu}} \Gamma(\mu) \cdot J_\nu(az)$$

Where $R(\nu + 2) > R(\mu)$ and $b > a$.

and Proceeding as before we find that

$$4 b^{a/2} J_{a/2}(b y^2) \cdot J_\nu \left\{ \frac{a \sqrt{y^4 + z^2}}{(y^4 + z^2)^{\frac{\nu}{2}}} \right\}$$

is self-reciprocal for transforms of order $R - \frac{1}{2}$ for different values of a, b, a and ν ; so that the above function represents a doubly infinite system of self-reciprocal functions for different values of a and ν .

Provided $R(\nu + 2) > R\left(\frac{a}{2}\right)$ and $b > a$.

Hence we get functions of two variables, representing sets of self-reciprocals, all belonging $R - \frac{1}{2}$. These functions may also be written as R_c .

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STUDIES IN COAGULATION

Part III. COAGULATION OF HYDROUS FERRIC OXIDE SOL BY POTASSIUM BROMATE AND POTASSIUM CHLORIDE

By

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(Read on 25th September 1956)

ABSTRACT

A sample of hydrous ferric oxide was peptized by hydrochloric acid and the sol thus obtained was dialysed to different extents of time to give sols of different purity. The variations in pH and the electrical conductance of the fresh as well as aged samples were noted in the presence of potassium bromate and potassium chloride solutions.

The results showed that there was an increase in pH and a decrease in the electrical conductivity, when the sols were treated by these electrolytes. The sol showed greater variations in pH in the presence of potassium bromate, when the values are compared with that of potassium chloride. It has been further noted that two months aged sols show greater variation in pH than the fresh samples. However, on extreme ageing pH of the sol samples fell considerably.

These results have been discussed with reference to the mechanism of coagulation of the hydrous ferric oxide sol.

In the part II of the series¹, we have reported that the sol of hydrous ferric oxide undergoes remarkable changes in pH during coagulation by potassium sulphate. Therefore it was thought necessary to study the effect of monovalent ions like BrO_3^- and Cl^- during the coagulation of the sol. Such investigations have been made with reference to the changes of hydrogen ion concentration and the electrical conductivity of the sol medium. It is well known that ageing plays an important role in the case of hydrous oxide sols, and therefore our studies have also been extended to the same samples aged for several months.

EXPERIMENTAL

Sols were prepared and studied in the manner reported earlier.¹ The results for such measurements are given in the following tables :

TABLE I SOL A

 $\text{Fe}_2\text{O}_3 = 0.2457$ gm. mole per litre

 $\text{Cl}^- = 0.07048$ gm. ion per litre

 $\text{Purity} = \text{Fe}_2\text{O}_3 / \text{Cl}^- = 3.568$

Volume of sol taken = 10 ml

Total volume = 20 ml

2N KBrO_3 in ml	pH			$(K_1 - K_2)$ in mhos $\times 10^4$		
	Fresh	2 months aged	8 months aged	Fresh	2 months aged	8 months aged
0	2.30	2.30	2.10	371.0	402.6	441.9
1	2.31	2.32	2.15	391.1	393.7	395.0
2	2.32	2.34	2.16	369.3	373.9	382.1
3	2.34	2.36	2.16	363.0	361.0	365.5
4	2.38	2.39	2.16	356.4	359.2	349.5
5	2.42	2.41	2.16	349.5	351.6	329.3
6	2.43	2.44	2.16	342.5	344.2	318.9
7	2.43	2.45	2.17	336.1	340.4	287.3
8	2.43	2.45	2.17	330.1	336.0	279.6
9	2.43	2.45	2.17	322.0	329.8	273.6
10	2.43	2.45	2.17	308.0	318.7	267.0

TABLE II SOL A₁
 $\text{Fe}_2\text{O}_3 = 0.2457$ gm. mole per litre

 $\text{Cl}^- = 0.0228$ gm. ion per litre

 $\text{Purity} = \text{Fe}_2\text{O}_3 / \text{Cl}^- = 10.780$

Volume of sol taken = 10 ml

Total volume = 20 ml

KBrO ₃ in ml 0.4N	pH			$(K_1 - K_2)$ in mhos $\times 10^4$		
	Fresh	2 months aged	8 months aged	Fresh	2 months aged	8 months aged
0	3.90	3.80	3.10	24.75	32.35	52.20
1	4.10	3.90	3.15	18.93	26.28	40.52
2	4.30	4.10	3.20	15.96	23.24	39.73
3	4.45	4.30	3.50	14.49	21.07	37.31
4	4.60	4.60	3.40	13.16	18.53	35.20
5	4.70	4.70	3.50	12.30	14.86	31.25
6	4.82	4.80	3.60	11.10	12.08	29.00
7	4.84	4.90	3.70	10.50	10.48	24.95
8	4.86	5.00	3.70	8.80	8.96	17.85
9	4.88	5.00	3.70	3.90	4.32	11.20
10	4.90	5.00	3.70	3.05	3.90	5.70

TABLE III SOL A

Volume of the sol taken=10 ml

Total volume =20 ml

4 N KCl in ml.	pH			(K_1-K_2) in mhos $\times 10^4$		
	Fresh	2 months aged	8 months aged	Fresh	2 months aged	8 months aged
0	2.30	2.30	2.10	371.0	402.6	441.9
1	2.30	2.31	2.11	370.4	400.0	425.2
2	2.31	2.32	2.12	340.8	391.2	404.3
4	2.32	2.34	2.14	332.2	372.7	395.0
5	2.34	2.36	2.15	277.2	346.5	388.4
5	2.35	2.37	2.15	264.2	321.1	373.6
6	2.37	2.38	2.15	260.0	310.2	369.2
7	2.38	2.39	2.15	244.6	300.6	355.8
8	2.39	2.40	2.15	236.1	289.9	345.4
9	2.40	2.41	2.15	218.8	274.4	339.8
10	2.40	2.41	2.15	205.7	261.5	320.0

TABLE IV SOL A₁

Volume of the sol taken=10 ml

Total volume =20 ml

0.8 N KCl in ml.	pH			(K_1-K_2) in mhos $\times 10^4$		
	Fresh	2 months aged	8 months aged	Fresh	2 months aged	8 months aged
0	3.90	3.8	3.1	24.75	32.35	52.20
1	4.10	3.9	3.3	18.82	27.68	45.58
2	4.30	4.1	3.4	16.93	24.79	40.30
3	4.60	4.4	3.5	14.12	22.14	36.78
4	4.70	4.6	3.55	12.06	20.19	32.82
5	4.72	4.8	3.6	10.88	18.00	29.15
6	4.74	4.9	3.6	8.64	14.30	26.00
7	4.76	4.9	3.6	7.35	13.46	22.44
8	4.78	4.9	3.6	6.08	12.93	18.56
9	4.80	4.9	3.6	5.68	10.38	14.06
10	4.80	4.9	3.6	4.14	8.17	10.93

In each table last three columns show the value of (K_1-K_2) , where K_1 is the specific conductivity of the mixture of the sol + electrolyte and K_2 is the specific conductivity of the electrolyte present in the mixture measured at 32°C.

DISCUSSION

The experimental data presented in tables I to IV show that during the addition of electrolytes to the sols, there is an increase in the alkalinity, which is related to the coagulating power of the electrolytes. If the sol is aged for two months, the liberation of alkali is enhanced considerably, and on extreme ageing the effect is not so pronounced. It should be mentioned here that Thomas and Whitehead² noted an increase in the pH value of the sol of alumina peptized by HCl on treatment with an electrolyte, like potassium sulphate. Similar results of the action of electrolytes have been reported by Thomas and coworkers³ in the case of hydrous oxide sols of alumina peptized by hydrobromic acid and thorium, beryllium and zirconium hydrous oxide peptized by hydrochloric acid.

Thomas and coworkers suggested that these hydroxide colloidal particles consisted of olated and possibly oxolated hydroxy compounds of Werner type, so that the increased pH value by the addition of neutral electrolytes to the sols could be attributed to the replacement of OH^- groups by the anions of added salt. This explanation for the increase of alkalinity observed during the coagulation does not appear probable, because X-ray analysis performed by Weiser and Milligan⁴ ruled out the formation of basic salts. Similarly Ghosh and coworkers⁵ have shown that there is no evidence of the formation of basic salt in the precipitation of hydrous oxides of iron, aluminium and chromium. The explanation advanced by Thomas and coworkers is inadequate in explaining the generation of alkali for the sols on the above grounds.

We have suggested the following picture of the mechanism of coagulation by an electrolyte in a previous paper⁶. When an electrolyte is added to a sol, the density of the diffused double layer of the oppositely charged ions, namely the anions is increased, so that it is attracted by the positively charged surface of the colloidal unit and finally its electrical charge is discharged. As a result of this the hydrogen ions, which are the stabilizing ions, now get adsorbed on the surface, causing an increase of the hydroxyl ion concentration of the solution.

The variations in pH show that for the same sol the alkalinity developed with potassium bromate is greater than potassium chloride. This variation is due to the difference in the grain size of the particles during their agglomeration leading to coagulation. According to Von Weimarn⁷ the grain size of a material is controlled by its rate of precipitation. It is, therefore, clear that the rate of coagulation with bromate being more rapid, the particles during agglomeration possess a more active surface, than that in the presence of potassium chloride, which coagulates the sol at a slower rate. Hence the adsorption of hydrogen ions becomes more pronounced with potassium bromate than with potassium chloride.

It is well known that on ageing hydrous ferric oxide loses its adsorptive capacity and chemical reactivity, but my experimental results show that a sol sample aged for two months produces more alkalinity than the corresponding sol when freshly prepared. Of course, when it is aged for eight months, the amount of alkali generated during its coagulation by electrolyte decreases considerably. Such results appear anomalous. We are, however, led to believe that hydrous ferric oxide is capable of adsorbing some hydroxyl ions as well, due to its amphoteric nature. But such active centres for the adsorption of hydroxyl ions more quickly decrease with age, in comparison to that for hydrogen ions⁸.

The electrical conductance has been calculated by taking the difference between the conductance of the mixture and the electrolyte added for coagulation studies. These data, may, therefore, be considered as the variation in the conduc-

tance of the sol by addition of electrolytes. It will be seen that the conductance of the sols usually decreases by the progressive addition of electrolytes. The decrease is due to the aggregation of the colloidal micelle, which also contributes to the electrical conductivity of the sol to a certain extent.

It should be noted here that though the pH variations observed in purer sol A, is greater, the actual decrease in the hydrogen ion concentration is more pronounced in the sol at a lower pH than the sol, which is at a higher one. This is due to the greater amount of hydrochloric acid in the sol at a lower pH, which imparts larger amounts of hydrogen ions, makes the colloidal particles smaller and gives greater surface to it. Moreover in the presence of larger amounts of acid more hydrogen ions are available to saturate the surface.

One of the authors (R. S. Rai) is thankful to the Ministry of Education, Government of India for the award of Senior Research Training Scholarship.

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STUDIES IN COAGULATION

PART V. COAGULATION OF TUNGSTIC ACID SOL

By

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(Read on 25th September 1956)

ABSTRACT

It has been observed that the fresh samples of tungstic acid sol always leaves some tungstic acid in the solution on coagulation, but the aged samples are completely coagulated by electrolytes. During the stepwise addition of neutral electrolytes, tungstic acid sol liberates acid. pH variations are greater for divalent ions and it follows the same order as their coagulating powers. The variations in pH proceed up to the coagulation point and beyond this point hydrogen ion concentration becomes stationary. The sol on ageing has a tendency to develop increased acidity. The measurements show that the electrical conductivity of the sol system diminishes continuously. These results have been explained by a new mechanism of coagulation.

Achar and Usher¹ observed the liberation of hydrogen ions, when a colloidal suspension of stearic acid was treated with a neutral salt. They ascribed it to be due to the progressive dissociation of the surface molecule of the colloidal particles. Bolam and Duncan² observed equivalence in ionic interchange in the case of both sulphur³ and stearic acid sol. We have investigated here the variation in hydrogen ion concentration of tungstic acid sol by the addition of electrolytes, because it has been considered to behave like stearic acid sol. *

Ghosh and Dhar⁴ suggested that this sol should behave as a colloidal electrolyte. It is well known that colloidal tungstic acid polymerise with age⁵. This led us to study the changes in the electrical conductivity of the sol system in presence of neutral electrolytes. Our investigations, have also been extended to study the effect of ageing on the variation of pH and electrical conductance of the colloid.

EXPERIMENTAL

A concentrated solution of A. R. Sodium tungstate was acidified with A. R. hydrochloric acid at 0°C till the precipitation was complete. Large excess of hydrochloric acid was avoided. The precipitate was washed by decantation several times until the liquid washings were free from chloride ions. The voluminous white gel was taken in a parchment bag and the dialysis continued for three weeks. The clear sol obtained was stored in jena glass bottles.

pH and specific conductivity were measured in presence of BaCl₂, CaCl₂, KCl, and NaCl exactly in the same way as given for hydrous ferric oxide sol⁶.

The results of such measurements are given in the following tables.
WO₃ = 3.48 gms./litre.

In the following tables 10 ml of the sol were taken each time and the total volume was made upto 20 ml by addition of water and electrolytes.

TABLE I

N/1000 Ba Cl ₂ in ml.	pH		(K ₁ - K ₂) in mhos × 10 ⁵	
	1 month aged	6 months aged	1 month aged	6 months aged
0	6.6	6.0	280.9	263.5
1	6.0	5.8	126.2	221.6
2	5.9	5.75	101.8	184.2
3	5.9	5.6	50.5	147.8
4	5.9	5.55	11.6	102.5
5	5.9	5.5	8.4	61.5
6	5.9	5.5	6.6	38.6
7	5.9	5.5	4.2	14.5
8	5.9	5.5	2.8	9.3
9	5.9	5.5	1.7	7.1
10	5.9	5.5	1.7	4.2

TABLE II

N/1000 Ca Cl ₂ in ml	pH		(K ₁ - K ₂) in mhos × 10 ⁵	
	1 month aged	6 months aged	1 month aged	6 months aged
0	6.6	6.00	280.9	263.5
1	6.4	5.90	268.0	236.9
2	6.3	5.80	246.8	215.9
3	6.2	5.75	237.4	191.5
4	6.1	5.75	230.4	156.0
5	6.1	5.70	220.0	123.2
6	6.1	5.65	194.3	114.6
7	6.1	5.65	160.6	108.7
8	6.1	5.65	128.1	93.5
9	6.1	5.65	100.7	86.8
10	6.1	5.65	91.2	70.7

TABLE III

N/100 KCl in ml.	pH		(K ₁ -K ₂) in mhos × 10 ⁵	
	1 month aged	6 months aged	1 month aged	6 months aged
0	6.6	6.0	280.9	253.5
1	6.2	5.85	220.9	253.0
2	6.15	5.7	210.5	211.6
3	6.15	5.68	203.9	180.4
4	6.1	5.65	197.0	170.0
5	6.1	5.65	172.7	143.6
6	6.1	5.65	156.4	118.9
7	6.1	5.65	120.7	105.0
8	6.1	5.65	105.7	98.1
9	6.1	5.65	92.5	81.7
10	6.1	5.65	61.0	72.8

TABLE IV

N/30 NaCl in ml.	pH		(K ₁ -K ₂) in mhos × 10 ⁵	
	1 month aged	6 months aged	1 month aged	6 months aged
0	6.6	6.0	280.9	263.5
1	6.1	5.7	243.6	239.6
2	6.1	5.65	228.4	218.1
3	6.1	5.65	203.5	186.2
4	6.1	5.65	188.7	172.5
5	6.1	5.65	175.3	150.0
6	6.1	5.65	152.1	135.6
7	6.1	5.65	134.5	112.7
8	6.1	5.65	115.6	101.0
9	6.1	5.65	94.7	90.6
10	6.1	5.65	79.7	73.5

In these tables K₁ stands for the specific conductivity of the sol and the added electrolyte and K₂ denotes the specific conductivity of the electrolyte added to the sol.

DISCUSSION

The experimental data presented here for the coagulation of tungstic acid sol clearly show that in all cases the pH of the sol medium decrease on the stepwise addition of mono-and bivalent electrolytes. When the variations in pH are compared for different electrolytes it will be seen that amount of acid generated with different electrolytes in general follows the same order as their coagulating powers. The result is very much similar to our observations already recorded for ferric oxide sol⁶. It has also been noted that the variations in pH proceed upto the coagulation point and beyond this hydrogen ion concentration becomes stationary.

The data given for the specific conductivity are the differences between the specific conductivity of the mixture and that of the added electrolytes. The measurements show that during the coagulation by different electrolytes the electrical conductivity of the sol system diminishes continuously. This is in agreement with the behaviour of hydrous ferric oxide sol.

The increase in the acidity of tungstic acid sol may be ascribed either (i) to the exchange of the stabilizing ions present in the mobile part of the double layer by the coagulating cations or (ii) may be explained according to our scheme of coagulation, which suggests the adsorption of OH^- ions by the colloidal surface⁶.

The conductometric measurement shows that during coagulation by different electrolytes, the electrical conductivity of the sol system diminishes continuously. This is due to the removal of the conducting micelles by their aggregation and also by their adsorption with the precipitating acid.

One of the authors (R. S. Rai) is thankful to the Ministry of Education, Government of India for the award of Senior Research Training Scholarship.

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STUDIES IN COAGULATION

PART VI. COAGULATION OF COLLOIDAL SILVER

By

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(Read on 25th September 1956)

ABSTRACT

Colloidal silver shows a decrease in the pH value, when electrolytes are added to coagulate it. The generation of acidity is more pronounced when the sol is coagulated by cation having higher valence. The electrical conductance of silver sol shows a remarkable decrease during its coagulation by electrolytes. These data have explained with reference to the mechanism of coagulation suggested here.

Colloidal silver is regarded to be formed by the preferential adsorption of hydroxyl ions by the particles and silver ions are the counter ions in the outer diffused layer surrounding the particles. The Bredig sol consists of silver particles with silver hydroxide in the intermicellar solution, while a Kohlschütter's sol can be obtained with pure silver oxide and hydrogen.¹ It is therefore evident that in both types of the sols, the stabilizing ions are OH⁻ ions which are adsorbed directly on the surface of silver particles, the presence of which has been confirmed by X-ray method.²

Silver sol is quite sensitive to electrolytes and coagulation experiments reveal that it bears a negative charge. In the earlier communications³ we have reported our results for hydrous ferric oxide and hydrous tungstic acid sols. We shall now describe the changes in pH and the electrical conductivity of the silver sol, effected by the addition of mono- and divalent electrolytes to the sol.

EXPERIMENTAL

Pure caustic soda solution was added to a silver nitrate solution and the precipitate was thoroughly washed until free from electrolytes. The precipitate was stored in a jena glass bottle and was warmed to 50–60°C and purified hydrogen gas was bubbled through the suspension for six hours. An intense yellow coloured fluorescent sol was formed, which was filtered through glass wool.

Total silver in the sol was estimated by Volhard's method and the pH and specific conductivity in the presence of NaNO₃, KNO₃, Ba(NO₃)₂ and Mg(NO₃)₂ were measured by the procedure already described in a previous paper³. The results are tabulated below.

TABLE I

Ag=1.18 gms per litre
 Volume of sol taken=10 ml
 Total volume=20 ml.

Electrolyte added in ml.	pH with			
	NaNO ₃ N/62.5	KNO ₃ N/80	Mg(NO ₃) ₂ N/900	Ba(NO ₃) ₂ N/1250
0	6.85	6.85	6.85	6.85
1	6.80	6.80	6.60	6.55
2	6.74	6.75	6.50	6.50
3	6.70	6.70	6.50	6.50
4	6.70	6.70	6.50	6.50
5	6.70	6.70	6.50	6.50
6	6.70	6.70	6.50	6.50
7	6.70	6.70	6.50	6.50
8	6.70	6.70	6.60	6.50
9	6.70	6.70	6.50	6.50
10	6.70	6.70	6.50	6.50

TABLE II

Electrolyte added in ml.	(K ₁ —K ₂) in mhos × 10 ⁶			
	Na NO ₃ N/62.5	KNO ₃ N/80	Mg (NO ₃) ₂ N/900	Ba (NO ₃) ₂ N/1250
0	222	222	222	222
1	156	128	181	210
2	130	117	156	191
3	110	110	140	182
4	98	85	126	178
5	87	71	116	160
6	71	65	101	129
7	68	60	87	110
8	66	56	84	101
9	63	51	82	96
10	60	50	80	91

In this table K₁ denotes the electrical conductivity of the sol and added electrolyte and K₂ stands for the specific conductivity of the added electrolyte.

DISCUSSION

In table I it will be seen that during the process of coagulation the acidity of the colloidal system increases by the addition of electrolytes and the decrease in the pH value of the colloidal system is a little more pronounced in the case, where the valency of the coagulating ions is large. It has already been stated that the stability of the negatively charged hydrous oxide sol is due to the preferential adsorption of OH^- ions. The process of the charge neutralization has been described by several authors⁴ as the replacement of the oppositely charged ions from the double layer, which is followed by charge neutralization on the surface of the coeloid itself. This view is untenable in the light of the above experimental results.

We have brought about a fact that with the process of charge neutralization by the oppositely charged ions, the colloidal surface has the capability of regaining the charge by the adsorption of similarly charged ions, if and when they are available in the system. It is for this reason that when an electrolyte is added to a negatively charged sol having the property of adsorbing OH^- ions the oppositely charged ions, which increase the amount of similar ions present in the double layer are not able to bring about charge neutralization instantaneously as postulated by Ghosh.⁵ Therefore during the charge neutralization process the colloidal particles have a tendency to regain the charge by the adsorption of oppositely charged ions by the system, thereby increasing the acidity.

A perusal of table II shows a remarkable decrease in the electrical conductivity of a silver sol, calculated by subtracting the conductivity of the added electrolyte from the observed values. Increase in the acidity of the system on the other hand should have shown an increase in the conductance. The results therefore, show that colloidal particles of silver contribute sufficient electrical conductivity to the system.

Our thanks are due to the Ministry of Education, Government of India for the award of a Senior Research Training Scholarship to one of us (R. S. Rai)

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COMPOSITION OF COMPLEXES IN THE SYSTEM $\text{HCl}-\text{Cl}_2$ FROM SOLUBILITY DATA

By

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ABSTRACT

For the system : $n\text{HCl} + \text{Cl}_2 \rightleftharpoons \text{H}_n\text{Cl}_{n+2}$, the expression :

$$n = \frac{\log(b-a)/(b'-a)}{\log c/c'}$$

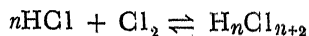
has been derived, where a and b represent respectively, the solubility of chlorine in water and hydrochloric acid solution of concentration c . The expression has been utilised to calculate the value of n from the data taken from London. It has been found that $n=1$ between 10° and 20°C , while at other temperatures the value of n is less than unity. Thus it appears that between the temperatures given above, the compound formed is HCl_3 , while at temperatures below 10°C or above 20°C higher polychlorides are probably formed.

In several publications Dey has advanced a new method (1) to utilise the solubility data to elucidate the composition of complexes formed by the dissolution of an insoluble material in a solution. He has derived certain mathematical expressions to calculate the composition from the solubility values in particular concentrations of the solvent solution. The method has been successfully employed to a study of the formation of polyiodides and polybromides (2) and to complex argentothiosulphates (3). The method of Dey was critically examined by Saraswat (4), and he applied the method to study complex formation in the system : silver phosphate—ammonia—water.

While considerable information is available in literature on the formation of poly-iodides and bromides, little is known about the polychlorides. Chlorine does not show an enhanced solubility in the presence of any soluble chloride except that of hydrogen. Draper (5) attributed the increased solubility of chlorine in hydrochloric acid solutions to the formation of HCl_2 , while Berthelot (6) assumed the compound formed to be HCl_3 .

London (7) determined the solubility of chlorine in water and in hydrochloric acid at various temperatures. In this paper his values have been utilised to calculate, the composition of the polychlorides formed in the solution, by the method of Dey.

Let us consider the reaction between hydrochloric acid and chlorine to be :



By the law of mass action :

$$\frac{[\text{Complex}]}{[\text{HCl}]^n[\text{Cl}_2]} = K \text{ (Stability constant)}$$

If b is the solubility of chlorine in hydrochloric acid solution of concentration c , and a the solubility of chlorine in water, then at the point of equilibrium,

$$[\text{Complex}] = (b-a)$$

$$\text{Cl}_2 = a$$

$$\text{HCl used} = n(b-a)$$

$$\text{HCl unused} = c - n(b-a)$$

$$\text{Therefore, } \frac{(b-a)}{(c-bn+an)^n a} = K$$

and for other corresponding concentrations a' , b' and c' ,

$$\frac{(b'-a')}{(c'-b'n+a'n)^n a'} = K$$

If $b-a = s$ and $b'-a' = s'$,

$$\frac{s}{(c-sn)^n a} = \frac{s'}{(c'-s'n)^n a} = K \quad (\text{as } a' = a)$$

or

$$\frac{s}{s'} = \left[\frac{(c-sn)}{(c'-s'n)} \right]^n$$

Taking logarithms of both sides we get,

$$\log \frac{s}{s'} = n \log \frac{(c-sn)}{(c'-s'n)} = n [\log (c-sn) - \log (c' - s'n)]$$

Expanding the right hand side in power series and neglecting the second and higher terms of the series we finally get,

$$\log \frac{s}{s'} = n \log \frac{c}{c'}$$

Therefore

$$\begin{aligned} n &= \frac{\log s/s'}{\log c/c'} \\ &= \frac{\log (b-a)/(b'-a)}{\log c/c'} \end{aligned}$$

It must be clearly understood that the expression is applicable only to associated complexes, where sn is smaller than c .

With the above expression we have calculated the value of n , from the data taken from London (7), and the results are shown in table I.

TABLE I

Solubility of chlorine in hydrochloric acid solutions at various temperatures

Temperature °C	Solubility coefficients			Value of <i>n</i>
	Water	Hydrochloric acid		
		Sp. gr. 1·046 2·583M	Sp. gr. 1·125 2·977M	
5	2·0	5·1	6·7	0·42
10	2·7	4·1	6·1	0·89
15	2·6	3·5	5·5	1·14
20	2·3	3·0	4·7	1·08
25	2·06	2·5	4·0	0·82

From the values of n calculated here, we conclude the possibility of the formation of HCl_3 between temperatures 10° to 20°C , where the value of n is unity. At temperature either below 10°C , or above 20°C , the value of n is less than unity, showing the formation of higher polychlorides.

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COMPOSITION OF ARGENTOTHIOSULPHATE COMPLEXES FROM SOLUBILITY DATA

THE SYSTEM $\text{AgCl}-\text{Na}_2\text{S}_2\text{O}_3-\text{H}_2\text{O}$

By

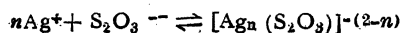
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ABSTRACT

The solubility of silver chloride in different solutions of sodium thiosulphate has been determined. A mathematical relation to calculate the value of n in the equation :



in terms of the solubility of silver chloride and the concentration of sodium thiosulphate, has been derived. The results show the formation of the complex ions $[\text{Ag}(\text{S}_2\text{O}_3)]^-$ and $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{--}$ in the system, the formation of each species depending upon the temperature and the concentration of thiosulphate.

The dissolution of silver halides in sodium thiosulphate solution is connected with the fixation of photographic negatives and the chemistry of the process has aroused considerable interest. Various compositions have been suggested for the complex argentothiosulphates formed in solution (1). The complex compounds have first been prepared by Herschel (2) and analysed by Lenz (3). The ammonium compound was isolated by Rosenheim and Steinhäuser (4). Among other workers on this problem are Richards and Faber (5), Schwicker (6), Schmidt (7), Luther (8) and Eder (9). Rosenheim and collaborators (10) also isolated an anhydrous product. The results of the analysis of the various workers are found to differ, probably because of the difficulty of obtaining the pure complex. The method of preparation adopted by the various authors is either of the following: (i) saturating a solution of sodium thiosulphate by silver chloride, (ii) adding ammoniacal silver nitrate to sodium thiosulphate and evaporation over sulphuric acid.

Baines (11) claimed to have obtained a pure variety of the complex by the addition of an aqueous silver carbonate suspension to a solution of sodium thiosulphate. He (12) obtained two complexes: $\text{Na}[\text{Ag}(\text{S}_2\text{O}_3)]$ and $\text{Na}_5[\text{Ag}_5(\text{S}_2\text{O}_3)_4] \cdot 2\text{H}_2\text{O}$. Basset and Lemon (13) found four different complexes in the system $\text{Ag}_2\text{S}_2\text{O}_3-\text{Na}_2\text{S}_2\text{O}_3-\text{H}_2\text{O}$.

In a publication from this laboratory, Dey and Mushran (14) reported the isolation of a product obtained by alcoholic precipitation from a solution of silver halide in sodium thiosulphate and determined the valency of the complex ion from the coagulation of a ferric hydroxide sol. Dey and Bhattacharya (15) observed that a precipitate of silver thiosulphate hydrolysed to silver sulphide in water and they utilised this fact for the quantitative determination of thiosulphate.

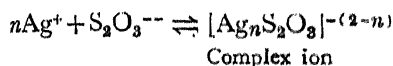
Luther and Leubner (16) studied the dissolution of silver chloride in sodium thiosulphate solutions. They assumed the formula of the complex and derived

certain mathematical expressions to calculate the equilibrium constant of the system. The values of the constants being satisfactory, they confirmed the postulated composition of the complex. In further communications, Dey (17, 18, 19) has advanced a new method for the calculation of the composition of complexes from solubility data and has used his calculations successfully to certain systems. In this paper the dissolution of silver chloride in sodium thiosulphate solutions of varying concentrations has been studied at different temperatures and the composition of the complex ions formed has been calculated with the help of expressions derived.

Silver chloride in water exists in the following equilibrium :



In a solution of silver chloride in sodium thiosulphate, the equilibrium can be represented by :



As silver ions go on dissolving in thiosulphate, the complex ions go on forming by the reaction between silver and thiosulphate ions and an equal number of chlorine ions are set free from silver chloride. So the removal of silver ions is guided by complex formation, leaving chlorine ions in excess.

At equilibrium in pure silver chloride solution :

$$[\text{Ag}^+][\text{Cl}^-] = K_s \text{ (Solubility product)}$$

Let us assume that a gram moles of silver have dissolved in a thiosulphate solution of concentration c gram moles.

Since Ag dissolved = a

Chlorine = $a + i$, where i is the solubility of silver chloride in water ; i is small in comparison to a , hence $\text{Cl} = a$

$$\text{and therefore concentration of free silver} = \frac{K_s}{[\text{Cl}]} = \frac{K_s}{a}$$

$$\text{Concentration of complex} = a/n$$

$$\text{Concentration of thiosulphate used to form the complex} = a/n$$

$$\text{Original concentration of the thiosulphate taken} = c$$

$$\text{Hence thiosulphate remaining free} = c - a/n$$

$$\frac{[\text{Complex}]}{[\text{Ag}^+][\text{S}_2\text{O}_3^{--}]} = K \text{ (Stability constant)}$$

If a_1 and a_2 are the concentrations of silver dissolved in c_1 and c_2 concentrations respectively of sodium thiosulphate :

$$\frac{(a_1/n)}{\left(\frac{K_s}{a_1}\right)^n \left(c_1 - \frac{a_1}{n}\right)} = K \quad \dots \quad \dots \quad \text{(i)}$$

$$\frac{(a_2/n)}{\left(\frac{K_s}{a_2}\right)^n \left(c_2 - \frac{a_2}{n}\right)} = K \quad \dots \quad \dots \quad \text{(ii)}$$

Simplifying we get,

$$\frac{a_1^{n+1}}{K_1^n (c_1 n + a_1)} = K \quad \dots \quad \dots \quad \text{(iii)}$$

and

$$\frac{a_2^{n+1}}{K_2^n (c_2 n + a_2)} = K \quad \dots \quad \dots \quad \text{(iv)}$$

Dividing (iii) by (iv) we have,

$$\left(\frac{a_1}{a_2} \right)^{n+1} = \frac{c_1 n + a_1}{c_2 n + a_2}$$

Taking logarithms of both sides we have,

$$(n+1) \log (a_1/a_2) = \log (c_1 n + a_1) - \log (c_2 n + a_2)$$

Expanding the right hand expression by logarithmic series we get,

$$\begin{aligned} (n+1) \log (a_1/a_2) &= \left[\log c_1 + \log n - \frac{a_1}{c_1 n} + \frac{1}{2} \frac{a_1^2}{c_1^2 n^2} - \frac{1}{3} \frac{a_1^3}{c_1^3 n^3} + \dots \right] \\ &- \left[\log c_2 + \log n - \frac{a_2}{c_2 n} + \frac{1}{2} \frac{a_2^2}{c_2^2 n^2} - \frac{1}{3} \frac{a_2^3}{c_2^3 n^3} + \dots \right] \\ &= \left[(\log c_1 - \log c_2) - \frac{1}{n} \left(\frac{a_1}{c_1} - \frac{a_2}{c_2} \right) - \frac{1}{3n^3} \left(\frac{a_1^3}{c_1^3} - \frac{a_2^3}{c_2^3} \right) \dots \right] \end{aligned}$$

The quantity $\left(\frac{a_1^3}{c_1^3} - \frac{a_2^3}{c_2^3} \right)$ and those involving higher powers are small and go on diminishing as we go further and may be neglected. Hence the equation ultimately reduces to :

$$(n+1) \log \left(\frac{a_1}{a_2} \right) = \log \left(\frac{c_1}{c_2} \right) = \frac{1}{n} \left(\frac{a_1}{c_1} - \frac{a_2}{c_2} \right)$$

Multiplying both sides by n we have,

$$n(n+1) \log \left(\frac{a_1}{a_2} \right) = n \log \left(\frac{c_1}{c_2} \right) - \left(\frac{a_1}{c_1} - \frac{a_2}{c_2} \right)$$

or

$$n^2 \log \left(\frac{a_1}{a_2} \right) + n \log \left(\frac{a_1}{a_2} \right) - n \log \left(\frac{c_1}{c_2} \right) + \left(\frac{a_1}{c_1} - \frac{a_2}{c_2} \right) = 0$$

or

$$\left[\log \left(\frac{a_1}{a_2} \right) \right] n^2 + \left[\log \left(\frac{c_1}{c_2} \right) - \log \left(\frac{c_1}{c_2} \right) \right] n + \left(\frac{a_1}{c_1} - \frac{a_2}{c_2} \right) =$$

Thus the expression reduces to an equation of the form :
 $ax^2 + bx + c = 0$, where x can easily be evaluated.

Hence

$$n = \frac{- \left\{ \log \frac{a_1}{a_2} - \log \frac{c_1}{c_2} \right\} \pm \sqrt{\left\{ \log \frac{a_1}{a_2} - \log \frac{c_1}{c_2} \right\}^2 - \left\{ 4 \log \frac{a_1}{a_2} \left(\frac{a_1}{c_1} - \frac{a_2}{c_2} \right) \right\}}}{2 \log \frac{a_1}{a_2}}$$

Thus the value of n can be calculated from a knowledge of the solubilities of silver chloride in known concentrations of sodium thiosulphate. This expression has been employed to calculate the composition of complex ions formed in a solution of silver chloride in sodium thiosulphate.

EXPERIMENTAL

A standard molar solution was prepared by dissolving AnlaR BDH sample of sodium thiosulphate in water and subsequent standardisation by the usual methods. Standard silver nitrate was prepared by dissolving AnalaR BDH sample in water and the strength checked by standard methods. All reagents employed were of analytical grade.

10 ml of 0.25M silver nitrate were taken in different test tubes and silver chloride precipitated in each case by the addition of hydrochloric acid. The precipitates were filtered and washed as usual, till free from chlorine ions. The filter paper cones containing the precipitate were punctured at the apex with a pointed glass rod and the precipitates received in 100 ml measuring flasks with the help of a jet of water from a wash bottle. Any precipitate that still remained adhering to the filter paper was also considered as will be seen later. A measured volume * of decinormal sodium thiosulphate solution was added to each flask and the volumes raised to 100 ml in each case. The flasks were maintained in a thermostat for four hours to attain equilibrium. The flasks were occasionally shaken to ensure dissolution of the precipitate. The undissolved precipitates were then filtered through funnels jacketed with water maintaining the temperature of the thermostat. The undissolved silver chloride was washed thoroughly with water and dried. The filter with the precipitate along with the corresponding punctured filter paper containing some adhering precipitate was then treated and silver chloride estimated gravimetrically as usual. Knowing the amounts of silver chloride taken initially, and that remaining undissolved, the amount dissolved in a particular concentration of thiosulphate was known.

The solubility of silver chloride in various concentrations of sodium thiosulphate was determined at different temperatures, and the value of n calculated as explained earlier. The results are presented in the following tables.

TABLE I

Temperature = 15°C

Final concentration of $\text{Na}_2\text{S}_2\text{O}_3$ (gmM)	AgCl dissolved (gm atoms of Ag)	Value of n
0.040	0.001570	..
0.035	0.001460	0.84
0.030	0.001340	0.79
0.025	0.001209	0.70
0.020	0.001060	0.70
0.015	0.000895	0.69
0.010	0.000701	0.67
0.005	0.000461	0.65

* The volume of the thiosulphate solution was so chosen, as to effect incomplete dissolution of the precipitate of silver chloride.

TABLE II

Temperature = 30°C

Final concentration of $\text{Na}_2\text{S}_2\text{O}_3$ (gmM)	AgCl dissolved (gm atoms of Ag)	Value of n
0.040	0.001982	...
0.035	0.001851	0.95
0.030	0.001700	0.81
0.025	0.001525	0.68
0.020	0.001331	0.64
0.015	0.001113	0.61
0.010	0.000930	0.59
0.005	0.000650	0.55

TABLE III

Temperature=40°C

Final concentration of $\text{Na}_2\text{S}_2\text{O}_3$ (gmM)	AgCl dissolved (gm atoms of Ag)	Value of n
0.040	0.001460	-
0.035	0.001282	0.52
0.030	0.001157	0.50
0.025	0.000953	0.50
0.020	0.000822	0.50
0.015	0.000676	0.47
0.010	0.000513	0.47
0.005	0.000301	0.36

The solubilities at temperatures higher than 40°C were not determined, as at higher temperatures, the undissolved precipitate of silver chloride gets coated with a layer of silver sulphide. The supernatant liquid has also a tendency to darken rapidly. At still higher temperatures, the dark liquid deposits a black powdery precipitate, probably of silver sulphide.

The filtrates in all the cases were colourless, but gradually changed colour to brown and finally to dark amber within the course of about twenty four hours. The darkening is more pronounced and rapid at higher temperatures and also in cases where the thiosulphate solution was dilute, viz., 0.010M and 0.005M. The dark liquid was colloidal and could be coagulated by ammonium nitrate.

An examination of tables I, II and III shows that the solubility of silver chloride in sodium thiosulphate is higher at 30°C, than either at 15°C or at 40°C. The value of n as shown in the last column also changes with temperature and with concentration of thiosulphate. The value of n at 15° and 30°C is approximately unity with higher concentrations of thiosulphate, and the value diminishes to 0.5 as the quantity of thiosulphate is decreased. At 40°C the value tends to remain equal to 0.5. The results therefore indicate the formation of $[\text{Ag}(\text{S}_2\text{O}_3)]^-$ when the concentration of thiosulphate is high, and that of $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{--}$, with lower concentrations of thiosulphate. At 40°C, however, the main product is the trivalent anion, and the monovalent complex ion is not formed.

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